Reaction mechanism of hydrogen generation from ammonia by DBD pulsed plasma

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In recent years, in order to reduce emissions of CO_2, construction of hydrogen energy society is desired. However, the problem of hydrogen society is the major energy loss in the transportation and the storage of hydrogen. In order to solve this problem, it is effective to use ammonia which is a hydrogen -rich substance as a hydrogen carrier. This study aims to find result for experimental study and the elementary reaction mechanism of hydrogen desorption reaction from ammonia in plasma conditions. As a result good agreement was obtained between the experimental and simulation values. And it was found that reaction rate of the reaction was very fast by plasma irradiation.

1. Introduction

In order to reduce emissions of CO_2, H_2 energy is introduced to the transport sector and the consumer sector. The CO_2 emission of those sectors in Japan is about 46%, but H_2 has energy loss for its transportation and storages[1)]. To resolve these problems, it is effective to accumulate and transports H_2 carrier before it converts to H_2[2)]. Particularly, NH_3 is expected as a H_2 energy carrier. NH_3 has a number of favorable characteristics, the primary one being its high capacity for H_2 storage, 17.6 wt%, based on its molecular structure. The secondary merit is that NH3 itself is carbon–free at the end users, although CO_2 emission on production of NH_3 is dependent on the source of energy.

We has developed a system for obtaining high-purity H_2 for fuel cells at atmospheric pressure plasma reactor with the high voltage electrode the H_2 separation membrane after the thermal decomposition of NH_3 using catalyst. This study has considered a search for experimental study and the elementary reaction mechanism of H_2 desorption reaction from NH_3 in plasma conditions. The purpose of this study is to estimate the behavior of NH_3 at that time, and research its elementary reaction mechanism.

2. Experimental setup

NH_3 is decomposed hydrogen and nitrogen by electric discharge energy from atmospheric plasma (Eq. 1). But we expect that H_2 conversion is changed by various factors. This research evaluates possibility for practical use as new H_2 production devices.

$$NH_3 + e \rightarrow 0.5\ N_2 + 1.5\ H_2 + e \quad \text{(Eq. 1)}$$

Fig. 1 shows experimental setup for H_2 production in a plasma reactor. First, NH_3 gas regulated mass flow controller is introduced into the plasma reactor, so that NH_3 gas is decomposed in atmospheric plasma generated by dielectric barrier discharge. In these experiments, the gases decomposed and generated by atmospheric plasma are analyzed by gas chromatography (GC) and quadrupole mass spectrometer (Q–Mass), so that we calculate H_2 conversion and H_2 production energy efficiency.

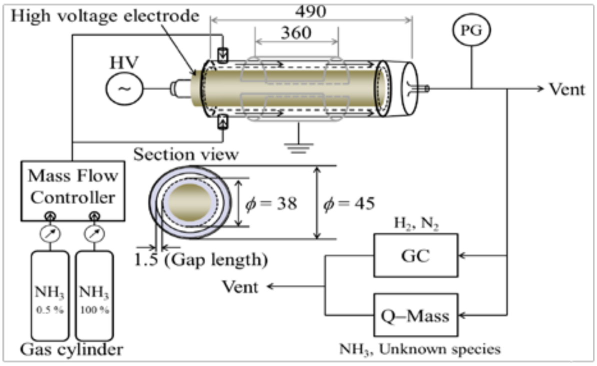

Fig.1 Experimental setup for H_2 production

3. Result

Fig. 2 shows the comparison between the H_2 selectivity in various flow rates and the power consumption when NH_3 conc. = 100%.

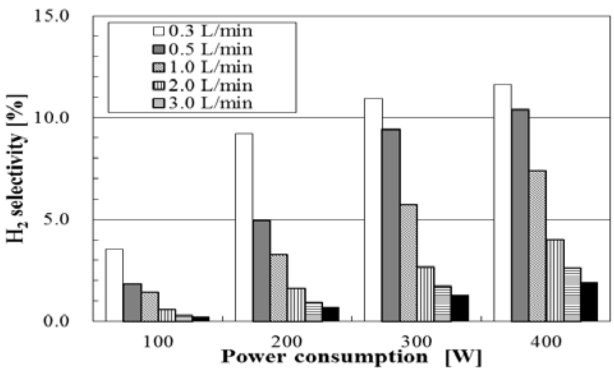

Fig. 2 Effects of power consumption and flow rates on H2 selectivity.

It was found that H_2 selectivity is increasing as the flow rate decreases or power consumption increases. Maximum H_2 selectivity was 7.5% when the flow rate is 0.3 L / min and power consumption is 400 W.

4. The Elementary Reaction and Analysis Method

CHEMKIN-PRO is used for the calculation, a chemical reaction analysis software of general purpose. Plasma-PSR-Reactor is used as a reactor model. H_2 is calculated for NH_3 conversion and gas phase reaction elementary reaction was prepared by combining the following elementary reactions:

1. The H / N based mechanisms for Mr. Skreiberg [3]
2. The H / N based mechanisms of Electron impact, ion and excitation species for Matzing [4]
3. The H / N based mechanisms of Electron impact, ion and excitation species for Starik [5]

Then, catalyst surface elementary reaction was using the original reaction is obtained by Mr. Bai.[6]

5. Analysis Result and Discussion

Fig. 3 shows the H_2 selectivity comparison between experimental and simulation results at flow rate = 3.0L/min and NH_3 conc. = 100%

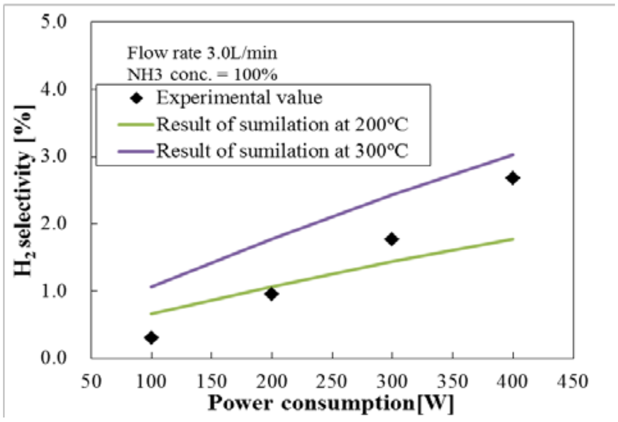

Fig. 3 PSR simulations result compared to the experimental result

There was an agreement with the experimental values in the following points. First, H_2 selectivity rate increases with the increase of power consumption. Second, gas temperature in the reactor at the time of plasma irradiation is 200ºC－300ºC; the temperature range is predicted from our previous study. Fig. 4 shows the reaction path diagram investigated from Analyze Reaction Paths of CHEMKIN- PRO. Therefore, Table 2 shows the main elementary reactions involving H_2 desorption reaction from NH_3 in plasma conditions.

Table 2 The main elementary reaction for NH_3 decomposition

R1	$NH_3+H=NH_2+H_2$	R4	$NH+H=N+H_2$
R2	$NH_3+E=NH+H_2+E$	R5	$NH_2+NH=N_2H_2+H$
R3	$NH_3+M=NH_2+H+M$	R6	$N_2H_2+H=NNH+H_2$

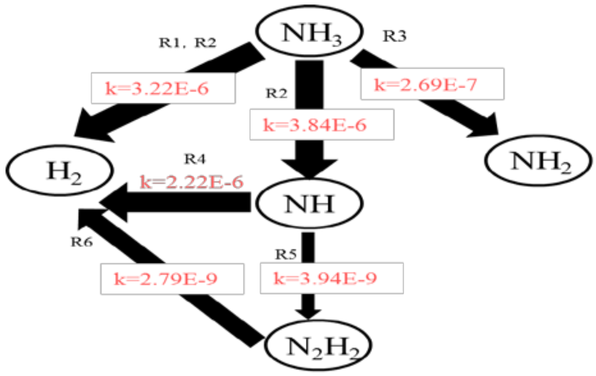

Fig. 4 Reaction path of H_2 product at 200 ºC.
($k = AT^n \exp(-E/RT)$)

It was found that the primary reaction of R1 and R2 or the successive reaction of R2→R4 are the main reaction of H_2 desorption reaction of NH_3. While the thermal decomposition, the reaction rate of R1 was about 10^{-17}, but the reaction rate is increased to 10^{-6} by irradiating plasma. The increasing of reaction rate is because the reaction was facilitated by plasma. In addition, the elementary reaction that greatly affects the H_2 selectivity of the elementary reaction of electron collision was R2. So, it is estimated that the primary reaction of R1 and R2 and the successive reaction of R2 →R4 are affected by plasma.

6. Conclusion

There was an agreement between simulation and experimental result. Both of them show the H_2 production rate is increased due to the increase in power consumption and the same gas temperature condition in the reactor while plasma irradiation (200ºC－300ºC). Therefore, analysis of reaction pathways found that hydrogen desorption kinetics of ammonia become 10^9 times faster than the usual thermal decomposition while using plasma.

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