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Short Communication

Ammonia decomposition to clean hydrogen using non-thermal atmospheric-pressure plasma

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ABSTRACT

The plasma decomposition of ammonia was studied as a function of applied voltage/power, residence time including length of an inner electrode and flow rate of reactant gases, partial pressure of ammonia, and amount and the metal species of the inner electrodes. The ammonia decomposition rates were in excellent agreement with the hydrogen production rates and no hydrazine production was detected, indicating the clean decomposition of ammonia in the current system. The decomposition rates were dependent on the applied power and the residence time and independent of metal species of the inner electrodes, in contrast to the strong dependence of the ammonia synthesis reaction on the metal species. A hydrogen yield of 100% was achieved with an applied power of approximately 50 W and a residence time of 1.2 s at ambient temperature and atmospheric pressure, with an applied voltage of 5 kV and a frequency of 50 kHz.

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Introduction

Ammonia is a very suitable material to use for the storage and transportation of energy because of its easy liquefaction under slight pressurization, the high level of hydrogen stored in each molecule, and the production of dinitrogen and water after use [1]. Methods for using ammonia as an energy carrier have thus become a major research objective and various new methods have been suggested for ammonia synthesis [2–6]. This is because the Haber-Bosch process, which is the main

industrial process used to synthesize ammonia, requires extreme reaction conditions, high temperatures and high pressures. Among ammonia's uses are as fuel in internal combustion engines [7,8] and fuel cells [9,10]. Another method involves converting the ammonia to hydrogen for use as a fuel, which can reduce the formation of nitrogen oxides. In this latter case, conversion techniques that allow for the effective decomposition of ammonia without creating any by-products should be developed. Although several heterogeneous catalysts that are capable of promoting such a

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conversion have recently been reported [11–15], they still have their drawbacks, such as high reaction temperatures and low conversion levels, which means more efficient techniques are required.

Recently, we reported that non-thermal atmospheric-pressure plasma was very effective for synthesizing ammonia at ambient temperatures, that the reaction was well catalyzed by inner electrodes [16], and that the order of the activity was $\text{Au} > \text{Pt} > \text{Pd} > \text{Ag} > \text{Cu} > \text{Fe} > \text{Mo} > \text{Ni} > \text{W} > \text{Ti} > \text{Al}$ [17]. These results demonstrated to us the possibility that the decomposition of ammonia, the reverse of the synthesis reaction, might similarly well proceed in plasma. Several studies have already reported the plasma decomposition of ammonia, which was well catalyzed by metals and oxides, but was frequently accompanied by the by-production of hydrazine [18,19], a possible obstacle to creating a fuel cell. We tried to introduce the clean decomposition of ammonia using our experimental method under specific reaction conditions. We observed satisfactory decomposition activity without the by-production of hydrazine. In addition, we found that the inner electrodes did not catalyze the decomposition activity, which is in contrast to the ammonia synthesis. These results were also useful for elucidating the kinetics of the plasma synthesis reaction of ammonia.

Experimental

A quartz reactor was used for the plasma experiments (Fig. S1). The outer diameter and thickness of the quartz tube were 12.7 mm and 1.0 mm, respectively, which were the same parameters used in previous studies [16,17]. The outside of the tube was surrounded by the outer electrode, which was a copper net. Various this, metal wires (wool-like) or rods were employed as the inner electrode. Wool-like metallic wires (summarized in Table S1) with surface areas of 61.3 cm² (for example, 1.10 g of Cu wool with a diameter of 0.08 mm) were employed as the inner electrode unless otherwise stated. The internal electrode was connected to a high voltage power supply, and the outer electrode acted as a grounded electrode. All experiments were performed at atmospheric pressure without heating. A mixture of NH₃ and N₂ (typically containing 4.87% NH₃) was allowed to flow into the reactor from the top of the reactor, and the exit gas was delivered into a diluted H₂SO₄ aqueous solution to gather any unreacted ammonia or hydrazine by-product. This gas was then sent to a gas chromatograph with a thermal conductivity detector and a molecular sieve MS-13X column to measure amounts of hydrogen. Typical reaction conditions included an applied voltage of 3–5 kV and a frequency of 50 kHz for the reaction port, which was 25–150 mm in length. The flow rate of the mixture was 100–200 mL min⁻¹ unless otherwise stated.

In order to perform the current reaction with high efficiency, feeding pure ammonia would be desirable, since all the power for plasma generation can be used for activation of ammonia. However, it should be considered that the gas volume largely changes before and after the ammonia decomposition reaction, and that the unreacted ammonia is trapped in the diluted H₂SO₄ aqueous solution after the reaction (which would cause complicated volume change in the

reactant gases). In addition, one cannot use any diluent gas (or an internal standard gas) such as helium because of a strong Penning effect. In order to solve these problems, we reduced the ammonia fraction to 4.87% and calculated the reaction rate by neglecting the volume change caused by the reaction. The ammonia decomposition rate and the hydrogen yield were calculated based on the ammonia molecules supplied as follows:

$$\text{Ammonia decomposition rate (\%)} = 100 \times \left\{ \frac{\text{conc. of NH}_3 \text{ supplied (mol min}^{-1}) - \text{conc. of NH}_3 \text{ detected at the outlet (mol min}^{-1})}{\text{conc. of NH}_3 \text{ supplied (mol min}^{-1})} \right\} \quad (1)$$

$$\text{Hydrogen yield (\%)} = 100 \times (2/3) \times \frac{\text{amount of hydrogen produced (mol min}^{-1})}{\text{conc. of NH}_3 \text{ supplied (mol min}^{-1})} \quad (2)$$

Results and discussion

Availability of the plasma decomposition of NH₃

The decomposition of ammonia using plasma was first studied as a function of the repetition of experimental runs using a Cu wool electrode since an increment in the activity of the ammonia synthesis rate was previously reported [16]. The conversion levels of NH₃ at the 1st, 2nd, and 3rd experiments were 70.8, 66.7, and 64.0%, respectively, where the applied voltage and the flow rate of the mixed gas were set at 4 kV and 200 mL min⁻¹, respectively, to decrease the conversion level of ammonia and clarify the change in the decomposition activity. A gradual decrease in the efficiency of the decomposition was observed with the repetitions. The experiments were accompanied by the formation of metallic spots, lines, and wafers on the inner wall of the silica tubular reactor, which was similar to those observed in the ammonia synthesis experiments [16]. The metal deposited on the silica wall was previously reported to be catalytically active for the ammonia synthesis [16], which explains the decreasing decomposition activity. The metals were catalyzing the synthesis of ammonia from H₂ produced by the decomposition and would become more active with increasing metal deposition. The results observed in the 1st experiments were used to compare the catalytic activity of the respective inner electrodes because the results of the 1st run were not influenced by the repetition or small changes in the surface states.

One of the objectives of the current study was to determine whether the plasma-aided decomposition of ammonia was suitable for producing clean hydrogen that does not contain any by-products, such as hydrazine. The current study's results were plotted in Fig. 1, which shows the correlation of the NH₃ decomposition rates with the H₂ production amounts. Note that all the data plotted in the figure were obtained at various experimental conditions on various electrodes, the details of which will be introduced in the next section. The excellent agreement of the two values within the range of experimental errors, regardless of which metal was used for inner electrodes and the experimental conditions, indicated that no side reactions, such as hydrazine synthesis or metal nitride formation, occurred. The absence of hydrazine was

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