Ammonia synthesis by synchronizing the pressure swing of N_2-H_2 plasma with the discharge timing and gas intake/exhaust cycles

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Abstract: We proposed a novel ammonia synthesis process in which the pressure of a N_2-H_2 nonthermal plasma system swung between low and high values to improve energy efficiency of the ammonia synthesis. In this study, we aimed to improve the synthesis efficiency by synchronizing the discharge timing to the pressure swing, and also synchronized the gas intake/exhaust timing. The results suggest the importance of synchronizing the discharge and intake/exhaust so that the synthesized ammonia is discharged from the catalyst surface.

Keywords: Ammonia Synthesis, Pressure Swing, Surface Discharge.

1. Introduction

Since ammonia is important not only as a hydrogen carrier but also as an alternative fuel to fossil fuels, highly efficient synthetic methods from renewable energy are demanded. Therefore, the importance of chemical conversion of electric power to synthesize ammonia by plasma technology is increasing significantly [1-6]. Basically, as is well known from Le Chatelier's principle, low-temperature and high-pressure conditions are thermodynamically preferable for ammonia synthesis from the feedstock of nitrogen and hydrogen molecules. However, in a practical industrial process, ammonia is produced by a high-temperature and high-pressure process because high temperature is kinetically necessary to break the strong triple bonds of nitrogen molecules. Therefore, ammonia is synthesized under a condition that is not thermodynamically optimal for an industrial process. The temperature dilemma appearing in such an endothermic reaction can be solved by using nonthermal plasma in many cases. In nonthermal plasma, the reaction rate is primarily determined by the electron temperature and less affected by the translational temperature of the reactant gas. Thus, it is possible to achieve a fast reaction rate kinetically while maintaining a low temperature that is thermodynamically favorable for endothermic reactions. Although the temperature dilemma appearing at ammonia synthesis process could be overcome by using nonthermal plasma, another dilemma arises at pressure of the reaction system. In nonthermal plasma, a low-pressure condition is essential to avoid arc transitions. Additionally, it is kinetically preferable to dissociate the nitrogen molecule effectively because generally electron energy is high when the pressure of the plasma system is low. However, high pressure is thermodynamically preferable for ammonia synthesis. To solve this dilemma of the pressure condition between thermodynamic and kinetic requirements for ammonia synthesis using nonthermal plasma, we proposed a novel ammonia synthesis process in which the N_2-H_2 plasma pressure swings from the low-pressure side wherein the nitrogen dissociation reaction is accelerated kinetically by high-energy electrons to the high-pressure side wherein the ammonia synthesis reaction is thermodynamically preferable. Additionally, the possibilities of enhancing desorption and adsorption of molecules on the catalyst surface by the pressure swing during ammonia synthesis can be speculated. If the rate-limiting step in ammonia synthesis is desorption of the product or adsorption of the reactant on the catalyst, the efficiency of ammonia synthesis can be improved by the pressure swing. In our previous study, the effect of pressure swing and discharge synchronization was confirmed for ammonia synthesis using N_2-H_2 plasma [7]. In this study, we aimed to improve the synthesis efficiency by synchronizing the discharge timing to the pressure swing, and also synchronized the gas intake/exhaust timing.

2. Experiment

In this study, a commercial diaphragm pump (APN-110KV-1, IWAKI) was modified as a pressure swing reactor in which N_2-H_2 plasma was created using a surface discharge system installed in the pump head. The compression ratio of the reactor was approximately 3, and the diameter of the diaphragm was approximately 74 mm. The pressure swing frequency was approximately 25 Hz and monitored by a pressure gauge. The surface discharge was created using a comb-shaped high-voltage copper electrode that was attached to the SiO_2 dielectric plate (30 mm × 30 mm × 0.5 mm). The high-voltage electrode was connected to a high voltage transformer (max. AC voltage: 11 kV, frequency: 18 kHz) controlled by the primary power source. The other side of the dielectric plate was covered by the ground electrode and attached to the reactor wall by sandwiching the ground electrode between the reactor wall and dielectric plate. The surface discharge was created on the dielectric plate near the edge of the comb-shaped electrode. Figures 1 and 2 show the schematic diagram of the experimental set-up and electrode configuration, respectively. The nitrogen and hydrogen feed rates were controlled by a mass flow controller (Model 3660, KOFLOC). Throughout this study, the total feed rate was maintained at 20 sccm and the ratio of N_2 and H_2 was 1:3. The ammonia in the reaction products was collected by a 4mM methanesulfonic acid trapping solution in an impinger glass tube installed at the outlet of the reactor and its concentratioin was analysed by the HPLC (EXTREMA, JASCO) with conductivity detector (CD-200, Shodex). The energy efficiency was calculated using the amount of ammonia produced and the energy consumed due to surface discharge. The energy consumed by the diaphragm pump was omitted in this calculation because it could be negligible when compared with the plasma energy consumed at a large scale. The energy consumed by the plasma was calculated using the Lissajous figure..

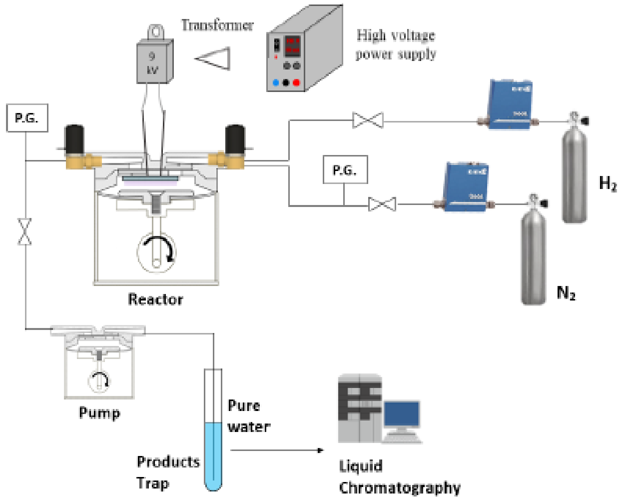

Fig. 1 Schematic diagram of the experimental set-up

3. Results and discussion

Fig.2 shows the experimental results for energy efficicency with synchronizing discharge timing and pressure swing (0.5-1.5 bar). Under conditions in which pressure swing and discharge were synchronized, the synthesis efficiency was improved by discharging only during the compression process. This suggested that it is important to turn off the discharge and remove ammonia from the catalyst surface before ammonia is decomposed. To confirm the importance of the desorption process, experiments were conducted to synchronize the intake and exhaust solenoid valves and the timing of pressure swings and discharges. The results showed that the synthesis efficiency was greatly improved by controlling the solenoid valves to accelerate the exhaust. These results clearly demonstrate the importance of actively exhausting the synthesized ammonia from the catalyst surface.

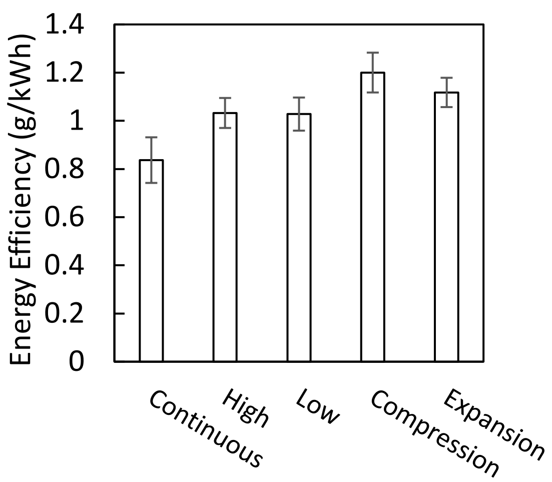

Fig. 2 Energy efficiency for NH_3 synthesis with various discharge timing

4. Conclusion

In this study, we attempted to improve the synthesis efficiency by synchronizing the discharge timing to the pressure fluctuation, as well as synchronizing the gas intake and exhaust timing. When pressure swing and discharge were synchronized, it was confirmed that the synthesis efficiency was improved by discharging only during the compression process. It was also found that controlling the solenoid valve to promote exhaustion significantly improved the synthesis efficiency. These results clearly demonstrate the importance of actively exhausting the synthesized ammonia from the catalyst surface.

5. References

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