Ammonia synthesis by pressure swing of N$_2$-H$_2$ plasma

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Abstract: We propose a novel ammonia synthesis process in which the pressure of N$_2$-H$_2$ plasma swings from low to high value. We have compared energy efficiency for ammonia synthesis between constant-pressure system and pressure-swing one. In case of constant-pressure system among 0.5 to 2.5 bar, the highest efficiency of 0.23 g-NH$_3$/kWh was obtained at the lowest pressure. The highest energy efficiency of 0.33 g-NH$_3$/kWh in this study was obtained by the pressure-swing system between 0.8-2.3 bar.

Keywords: Ammonia synthesis, Pressure-swing, Surface discharge

1. Introduction

Ammonia is industrially important compound and consumes huge amount of energy in its production process. Therefore an improvement of ammonia synthesis efficiency has a large impact on the global environment and a lot of related studies have been reported [1-3]. As is well known from Le Chatelier’s principle, low-temperature and high-pressure condition is preferable for the ammonia synthesis from nitrogen and hydrogen molecules. However, in industrial process ammonia is produced by a high-temperature and high-pressure process. This is because high temperature is necessary to break strong triple bond of nitrogen molecules. On the other hand, nitrogen molecule can be dissociated by electron impact reactions in non-thermal plasma even though the translational gas temperature is very low. In non-thermal plasma, however, low-pressure is preferable to dissociate nitrogen molecule because electron energy is higher when the pressure of the plasma system is lower. In order to overcome this dilemma in optimum pressure between thermodynamic and kinetic requirements for ammonia synthesis by non-thermal plasma, we propose here a novel ammonia synthesis process. In this process, the pressure of N$_2$-H$_2$ plasma swings from low-pressure side where the nitrogen dissociation reaction is accelerated to high-pressure side where the ammonia synthesis reaction is promoted.

2. Experimental

In this study, a commercial diaphragm pump was applied as a pressure-swing reactor in which N$_2$-H$_2$ plasma is created by a surface discharge. The compression ratio of the reactor is about 3 and the diameter of the diaphragm is about 74 mm. The pressure-swing frequency is able to be changed from 40 to 120 Hz. The surface discharge is created by a comb-shaped high-voltage copper electrode which is attached to the SiO$_2$ dielectric plate (30 mm x 30 mm x 0.5 mm). The high-voltage electrode was connected to the high voltage transformer (max. AC voltage: 11 kV, frequency: 18 kHz) controlled by the primary power source. Another side of the dielectric plate is covered by the ground electrode and attached to the reactor wall. The surface discharge is created on the dielectric plate near the edge of comb-shaped electrode. The reaction products were collected by a liquid-nitrogen cold-trap installed at the outlet of the reactor. The product amount was calculated by the pressure rise after removing the cold trap and the volume of the cold trap. The composition of the reaction product is analysed by a quadru-pole mass spectrometer and only the product detected in this study was ammonia.

3. Results and discussion

Experimental results to explain the pressure-swing effect are shown in Figure 1. In this figure, experimental results with constant-pressure system are also indicated as well as that with pressure-swing system. Among constant-
pressure system results, the highest efficiency of 0.23 g-NH₃/kWh was obtained at the lowest pressure condition, which reveals our reaction system to be more kinetically dominated system rather than thermodynamically controlled one. The highest energy efficiency of 0.33 g-NH₃/kWh was obtained by the pressure-swing system between 0.82-2.34 bar.

We have also investigated the influence of pumping frequency on the energy efficiency for ammonia synthesis. Figure 2 shows dependence of energy efficiency for ammonia synthesis on the pressure-swing frequency between 40 to 120 Hz. As shown in Figure 2, the dependence of energy efficiency on the pumping frequency was not clearly seen in the frequency range we tested. However, pressure-swing system always shows higher energy efficiency as compared with constant-pressure system.

4. Conclusion

We have fabricated a pressure-swing plasma reactor in which N₂-H₂ DBD plasma was created and ammonia was synthesized. We have compared energy efficiency for ammonia synthesis between constant-pressure system and pressure-swing one. In case of constant-pressure system between 0.5 to 2.5 bar, the highest efficiency of 0.23 g-NH₃/kWh was obtained at the lowest pressure. The highest energy efficiency of 0.33g-NH₃/kWh in this study was obtained by the pressure-swing system between 0.82-2.34 bar. We have also investigated the influence of pumping frequency on the energy efficiency for ammonia synthesis. Although the dependence on the pumping frequency was not clearly seen in the frequency range we tested, pressure-swing system always shows higher energy efficiency as compared with constant-pressure system.

5. References