Catalytic activity of metal electrodes for ammonia synthesis from N_2 and H_2 in atmospheric-pressure non-thermal plasma

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INTRODUCTION

Ammonia NH_3 is a potential candidate as energy carriers because it can be easily liquefied and has the large amount of hydrogen stored in each molecule. Since the current Harbor-Bosch process consumes much energy, new NH_3 synthesis methods have attracted significant attention. Recently, we found that the inner copper electrode used for plasma generation works as the catalyst for an NH_3 synthesis and the activity is greatly improved by repetition of experiments [1]. In this study, we examined the catalytic activity of various metal electrodes. The decomposition was also measured to analyze the kinetics of NH_3 synthesis. Furthermore, the factors controlling the activity were investigated using Gaussian09.

RESULTS AND DISCUSSION

The activity of wool-like metal electrodes was studied as a function of number of experiments. Activity of Pt, Pd, Ag, Cu, and Ni increased with the repetition of experiments, while those of Au, Fe, Mo, W, Ti, and Al were almost constant. The increase in the former group was due to deposition of metal on inner wall of the silica tube. The NH_3 synthesis rate (r_{NH3}) in the first experiment was Au > Pt > Pd > Ag > Cu > Fe > Mo > Ni > W > Ti > Al. The NH_3 yield on Au was 1.8% at H_2/N_2=1. The formation energy (ΔE_f) of the metal nitride, M_3N, was calculated with Gaussian09. As shown in Fig. 1, the catalytic activity was dependent on ΔE_f, and higher M_3N formation energy would be suitable for the NH_3 synthesis.

NH_3 decomposition was also investigated as a function of material, shape (rod or wool), length of electrode, deposition of metals on silica, applied voltage, and flow rate (Fig. 2). The decomposition was dependent on applied voltage and residence time, but did not depend on the electrode material nor the shape, indicating that NH_3 decomposition proceeded in a plasma phase and the meal electrode did not work as a catalyst. The kinetics of NH_3 synthesis rates were well analyzed on these hypotheses. Emission spectra of excited nitrogen molecules in plasma were measured but did not give any correlation with the catalytic activity.

CONCLUSIONS

The remarkable catalysis of the electrode materials for the NH_3 synthesis was found in atmospheric-pressure non-thermal plasma. The activity was well correlated with the formation energy of metal nitride, M_3N.

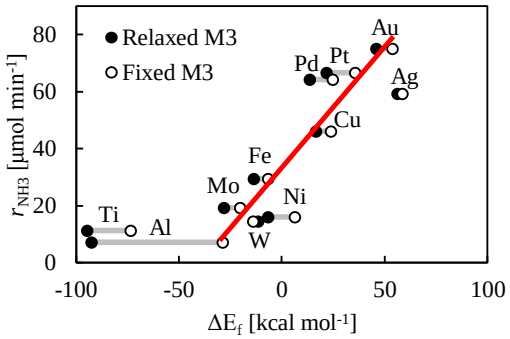

Fig. 1. Correlation of r_{NH3} and ΔE_f. r_{NH3} was measured at applied voltage 5 kV, frequency 50 kHz, electrode area 61.3 cm^2, total flow rate 100 ml min^{-1}, and H_2/N_2 = 1.

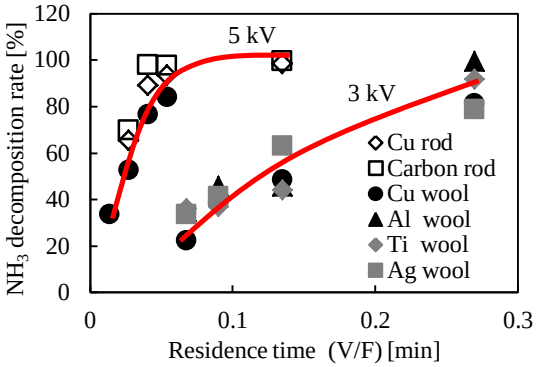

Fig. 2. Change in NH_3 decomposition rate with applied voltage, residence time, and electrode material. Measurement was performed at applied voltage 3 or 5 kV, frequency 50 kHz, electrode length 15-150 mm, total flow rate 50-200 ml min^{-1}, and NH_3 4.68% (N_2 balance).

REFERENCES

[1] K. Aihara, M. Akiyama, *et al.*, Chem. Commun., 52 (2016) 13560.