

# Wool-like Au, Pt, Pd, Ag, or Cu electrodes as active catalysts for ammonia synthesis in nonthermal atmospheric-pressure plasma of N<sub>2</sub> and H<sub>2</sub>

**Masakazu Iwamoto,<sup>a,\*</sup> Mao Akiyama,<sup>b</sup> Keigo Aihara,<sup>b</sup> and Takashi Deguchi<sup>b</sup>**

<sup>a</sup> *Research Institute for Sci. and Eng., Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan.*

<sup>b</sup> *Research and Development Initiative, Chuo University, 1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan.*

*\*Corresponding author: Fax number +81-5286-3115, E-mail address iwamotom@aoni.waseda.jp*

**Abstract:** Wool-like metal electrodes of Au, Pt, Pd, Ag, or Cu gave ammonia yields of 2.5-3.5% at H<sub>2</sub>/N<sub>2</sub>=3 in nonthermal plasma under atmospheric pressure without heating. DFT calculations indicated that a more unstable M<sub>3</sub>N intermediate produced higher catalytic activity. The N<sub>2</sub>/H<sub>2</sub> ratio dependence and formation rate constants of ammonia on the catalysts were different from those for the conventional Haber-Bosch process. The decomposition of ammonia proceeded in a plasma-irradiated gas phase.

**Keywords:** Ammonia Synthesis, Nonthermal Plasma, Gold.

## 1. Introduction

A new synthesis method for ammonia is strongly desired from an energy-saving perspective because the Haber-Bosch process consumes 1-2% of the world's annual primary supply. In addition, one of the significant challenges with hydrogen use is the storage and transportation of hydrogen. Ammonia is very suitable for storage and transportation because of its easy liquefaction under slight pressurization, the high level of hydrogen stored in a molecule, and the production of dinitrogen and water after use. Active studies have been continued using newly developed catalysts in a heterogeneous phase, metal complex catalysts in a homogeneous phase, electrochemical synthesis in an aqueous solution, and synthesis with plasma irradiation. In the plasma-assisted catalysis, a nonthermal atmospheric plasma was applied to synthesize ammonia, and catalyst-loaded ceramic membranes were used to obtain yields of approximately 2%. However, these have disadvantages of slow production rates due to the slow flowing velocity of the reactant gases. No experimental result, except for the metal wool catalysis in our previous report,<sup>1-3</sup> could provide a useful and novel strategy or approach for ammonia synthesis that might be superior to the current Haber-Bosch process. High catalytic activity of gold and others will be demonstrated in this study; and a DFT calculation will indicate the factor determining the catalytic activity. The results will be significant for achieving future progress in an ammonia synthesis and hydrogen society.

## 2. Experimental

The outer diameter and thickness of the quartz tube reactor were 12.7 mm and 1.0 mm. The outer side of the reactor was surrounded by the outer electrode. Various metal thin-wires (wool) with surface areas of 61.3 cm<sup>2</sup> were employed as the inner electrode, which was connected to a high voltage power supply. A mixture of N<sub>2</sub> and H<sub>2</sub> (H<sub>2</sub>/N<sub>2</sub>=1 and 100 mL min<sup>-1</sup> unless otherwise stated) was flowed into the reactor at atmospheric pressure without heating, and the exit gas was delivered to a diluted H<sub>2</sub>SO<sub>4</sub> aqueous solution to gather ammonia. Typical reaction conditions included an applied voltage of 5 kV and a frequency of 50 kHz for the reaction port, which was 150 mm in length. The yields of ammonia varied with the repetition of experiments, and the results observed in the first experiment were used to compare the catalytic activity of the respective metals because they were the values with no influence on the repetition or little change in the surface states.

## 3. Results and discussion

The ammonia yield substantially increased when Pt, Pd, Ag, Cu, and Ni wools were repeatedly used as electrodes. The activity of Au, Fe, Mo, Ti, W, and Al was approximately constant during the experiments. The increases in activity resulted from metal deposited on the inner wall of silica tube. The order of the

initial catalytic activity was  $\text{Au} > \text{Pt} > \text{Pd} > \text{Ag} > \text{Cu} > \text{Fe} > \text{Mo} > \text{Ni} > \text{W} > \text{Ti} > \text{Al}$ , indicating that the gold wools exhibited the highest activity for ammonia synthesis. The activity of the metal catalysts for ammonia synthesis in plasma greatly differed from that of the Haber-Bosch process because of the difference between the activation of  $\text{N}_2$  in the conventional heterogeneous catalysis and that in the plasma.

To identify the reasons for the high activity of gold and others, energy changes in the surface nitride formation  $\Delta E_f$  were calculated using a DFT calculation (Gaussian 09 with the Hamiltonian B3LYP) on various metals. An  $\text{M}_3$  cluster (M=an electrode metal atom) was employed as a minimum model of the catalyst surface. The reaction energy without zero-point energy correction was calculated using the self-consistent field energies of the molecules of a complex, cluster, and substrate.

In Figure 1, the initial catalytic activity is plotted as a function of  $\Delta E_f$  where the results of the relaxed and frozen  $\text{M}_3\text{N}$  were both employed. One can recognize a fair linear correlation between the  $\Delta E_f$  and catalytic activity. The more instable  $\text{M}_3\text{N}$  had a better ammonia yield. The correlation indicated the first step of the current plasma synthesis of ammonia, the reaction of an activated nitrogen molecule with the electrode surface, would be the most important, rate-limiting step for the catalysis.

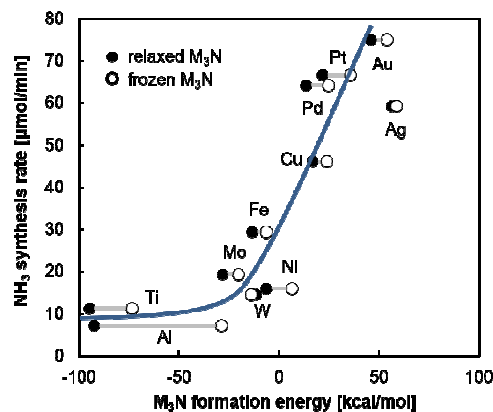
Emission spectra were measured during the plasma reaction to observe active species for the  $\text{NH}_3$  synthesis. A very intense second positive band from an activated neutral nitrogen molecule  $\text{N}_2^*$  was observed with various weak bands. In the current experiments, the intensity of  $\text{N}_2^+$  emission bands was far lower than that of  $\text{N}_2^*$ . All of these bands increased with the increasing applied voltage and decreased with the introduction of  $\text{H}_2$ . Plasma activation of nitrogen molecules roughly depended on the waveform, frequency, voltage, and current of plasma instead of on the metal species of electrodes. The results suggested that the generation of the  $\text{N}_2^*$  species was independent of metal species used as the electrodes and the metal types would strongly affect the reaction of generated  $\text{N}_2^*$  species with the metal surface.

The ammonia yield on gold or copper wools was examined as a function of the molar ratio of  $\text{H}_2$  and  $\text{N}_2$ . The correlation was analyzed using the following kinetic equation,  $r_{\text{NH}_3} = kP_{\text{H}_2}^\alpha P_{\text{N}_2}^\beta$ .  $\alpha(\text{Au})=1.50$  and  $\beta(\text{Au})=1.46$ , and  $\alpha(\text{Cu})=1.51$  and  $\beta(\text{Cu})=0.17$  were obtained. These values differed from those reported on well-known solid catalysts ( $\alpha=1.5-2.2$  and  $\beta=0.9-1.2$  on Fe, and  $\alpha=-0.43$  and  $\beta=1.0$  on Ru-Cs/MgO). The changes in the partial pressure dependences with the metal and repetition of experiments were recognized, but detailed discussion would require in-depth understanding of the reaction mechanisms. The positive values on the partial pressure of hydrogen on Au and Cu catalysts are significant for the practical application of the current method because the increase in the hydrogen partial pressure would not result in a decrease in the ammonia formation rate. Finally the production rate of ammonia was studied as a function of the residence time of the reactant gases. The formation rate of  $\text{NH}_3$  on the fresh Cu was smaller than that on Au, and the decomposition rate constant on the fresh Cu was the same as that on Au, resulting in the low activity of Cu for ammonia synthesis in the plasma system. Interestingly, all decomposition rate constants determined here are approximately coincident. This might suggest progress of the decomposition reaction of ammonia in a plasma-irradiated gas phase.

In conclusions, the current results pave the way for a new approach to ammonia synthesis that may be significant for future hydrogen applications.

## References

1. K. Aihara, M. Akiyama, T. Deguchi, M. Tanaka, R. Hagiwara, M. Iwamoto, *Chem. Commun.*, **2016**, 52, 13560.
2. M. Iwamoto, M. Akiyama, K. Aihara, T. Deguchi, *ACS Catal.*, **2017**, 7, 6924.
3. M. Akiyama, K. Aihara, M. Matsukata, M. Iwamoto, *Int. J. Hydrogen Energy*, submitted.



**Figure 1.** Dependence of the initial activity of various metal wool catalysts for ammonia synthesis on the formation energy of tri-nuclear nitride  $\text{M}_3\text{N}$ .