NH_3 synthesis using combination of Ru catalyst, hydrogen-permeable membrane, and phosphate electrolyte from N_2 and H_2O by electricity.

Kanako Imamura,[a] **Jun Kubota**[a*]

[a]*Department of Chemical Engineering, Fukuoka University, Fukuoka, 814-0180, Japan*
**Corresponding author: +81-92-865-6031, jkubota@fukuoka-u.ac.jp*

Abstract: A new NH_3 synthesis devise with a combination of Ru catalysts, hydrogen-permeable membranes, and phosphate electrolytes from N_2, H_2O, and electricity has been investigated. The CsH_2PO_4-based electrolyte was operated at 250°C for splitting water between a Pd-Ag membrane and Pt anode by electrolysis. Hydrogen in the Pd-Ag membrane was extracted from the back-side of membrane to form NH_3 by the Ru-catalyst. This devise synthesized NH_3 with the rate of 9×10^{-10} mol s^{-1} cm^{-2} at current density of 10 mA cm^{-2}. Kinetics of NH_3 synthesis is discussed in this presentation.

Keywords: Ammonia synthesis, electrolysis of water, energy carriers

1. Introduction

Ammonia synthesis is one of the largest chemical process in the modern society, which is utilized for the production of artificial fertilizers to maintain the human life. Most of NH_3 is currently synthesized from H_2 based on fossil resources, and the energy of H_2 production for NH_3 synthesis is considerable. Recently, NH_3 attracts attention as an energy carrier because it has high hydrogen density, flammability in combustion engines, and applications to direct fuel-cells. When NH_3 is synthesized from renewable energies, it would be a promising technology for future human society. Even using conventional technologies, NH_3 can be synthesized from the combination between water electrolysis to produce H_2 from renewable energy sources and NH_3 synthesis from H_2. However, water splitting is large endothermic reaction and NH_3 synthesis from H_2 is large exothermic reaction. If water electrolysis and NH_3 synthesis are operated separately without heat exchange, this energy loss is remarkable. The combination of electrolysis and NH_3 synthesis in a single devise in thermal equilibrium can compensate the endothermic and exothermic heats in the respective reaction steps. In this manner, electrochemical synthesis of NH_3 from N_2 and H_2O by electricity is a notable method to produce NH_3 by minimum electricity[1] and numerous attempts has been reported quite recently[2,3].

Electrochemical synthesis of NH_3, however, has many disadvantages. The produced NH_3 is easily absorbed into proton-conductive electrolytes, and the moisture for both electrodes easily poisons the active sites of NH_3 catalysts and easily attaches to NH_3 to form aqueous NH_3. To avoid these disadvantages, we propose the NH_3 synthesis devise with a combination of Ru catalysts, hydrogen-permeable membranes, and phosphate electrolytes as illustrated in Figure. 1. The NH_3 synthesis is driven without any electrochemical potential, but the chemical potential of hydrogen atoms on the NH_3 catalyst is strongly influenced by the chemical potential of hydrogen atoms in hydrogen-permeable membranes which is controlled by the electrochemical potential of hydrogen-permeable membranes. The kinetic properties of the present devise are object of discussion.

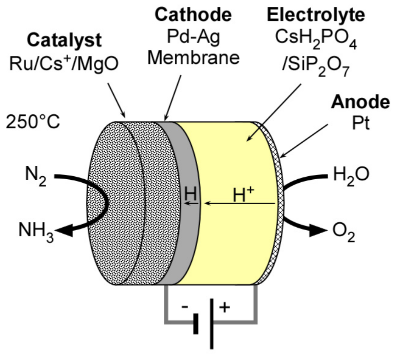

Figure 1. Schematic drawing of NH_3 synthesis using Ru catalysts, hydrogen-permeable membranes, and phosphate electrolytes from N_2, H_2O, and electricity

2. Experimental

The cell consisted of 600 mg of 2 wt%-Ru/Cs^+/MgO (Ru/Cs^+=1 mol) catalyst, Pd-Ag (25 mol%-Ag) membrane of 100 µm thick, CsH_2PO_4/SiP_2O_7 electrolyte, and Pt paste. The apparent cell diameter was 20 mm. They are held in a vessels made of SUS. N_2 gas was fed to the Ru catalyst side at the stated flow rate and Ar gas of 10 cm^3-STP min^{-1} with humidification of

16 μL liquid-H_2O min^{-1} was supplied to the anode side. The exhaust gas from Ru catalyst side was introduced into 1.0 mM H_2SO_4 to collect produced NH_3 and amount of NH_3 was estimated from the electric conductivity of solution. Simultaneously, the exhaust gas was analyzed by a gas chromatograph to estimate the production of H_2. 2 wt%-Ru/Cs^+/MgO was pretreated by flow of mixture of N_2 and H_2 at 250°C in prior to the NH_3 synthesis with electrolysis.

3. Results and discussion

The formation of NH_3 at the N_2 flow rate of 3 cm^3-STP min^{-1}, electrolysis current of 10 mA cm^{-2}, and various cell temperatures are shown in Figure 2. NH_3 was monotonically produced from the cathode side and the rate of 9.0×10^{-10} mol s^{-1} cm^{-2} was obtained at 250°C. 9.0×10^{-10} mol s^{-1} equals to 3.2 μmol h^{-1}. The current efficiency for NH_3 was estimated to be 2.6%, and the other part was found to be used for H_2 production. Arrhenius plots are shown in Figure 3. The NH_3 formation at 3.2 mA cm^{-2} and that from the 3 H_2 + N_2 flow in the cathode side without electrolysis are also shown in Figure 3. The apparent activation energies for the NH_3 formation at 3.2 and 10 mA cm^{-2} were estimated to be 69 and 93 kJ mol^{-1}, respectively. They were somewhat smaller than that from the 3 H_2 + N_2 flow without electrolysis. It was considered that the NH_3 synthesis from N_2 and water electrolysis was operated under N_2-rich conditions resulting in the small apparent activation energies because of less hydrogen poisoning[4]. In Figure 3, it should be noted that the Arrhenius plots for NH_3 synthesis from N_2 and water electrolysis are deviated from the straight lines at high temperature. The calculation of chemical equilibrium showed that the chemical equilibrium contributed the formation rate of NH_3 of ammonia in the high temperature region.

The dependence of rate of NH_3 formation on the rate of N_2 flow indicated that the NH_3 synthesis was poisoned by the presence of H_2, so that the N_2 flow rate was much higher than the stoichiometric rate of H_2 production at the maximum NH_3 formation rate. The detailed discussion on the kinetical properties and the strategies for the improvement of devise is shown in this presentation.

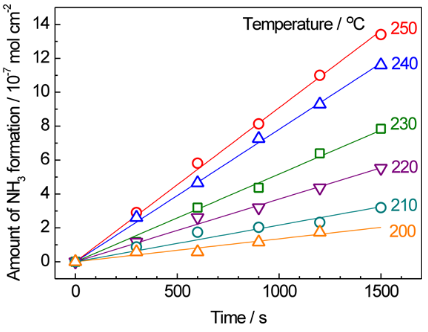

Figure 2. NH_3 formation using Ru catalysts, hydrogen-permeable membranes, and phosphate electrolytes from N_2, H_2O, and electricity at various temperatures. The current was 10 mA cm^{-2}.

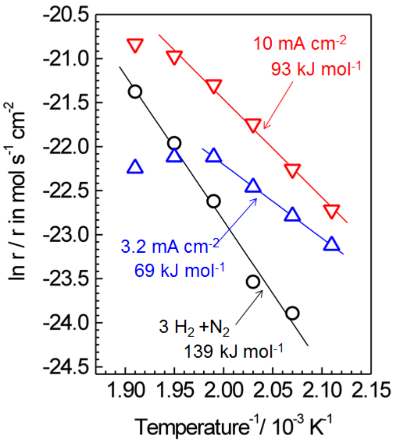

Figure 3. Arrhenius plots of rates of NH_3 formation at 3.2 (△) and 10 mA cm^{-2} (▽) and N_2 flows of 1 and 3 cm^3-STP min^{-1}, respectively. The rates of NH_3 formation from mixture gas of 3 H_2 + N_2 are also shown as open circles (○).

4. Conclusions

The combination of Ru catalysts, hydrogen-permeable membranes, and phosphate electrolytes was examined for NH_3 synthesis from N_2 and H_2O by electricity, and the rate of NH_3 formation of 9.0×10^{-10} mol s^{-1} cm^{-2} with a current efficiency of 2.6% was obtained at 250°C. The challenges in the present devise has been discussed.

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References

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