

Ammonia production by HNO₃ generated from NO_x

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ABSTRACT

The efficient ammonia synthesis at a low temperature and an atmospheric pressure are desired to storage hydrogen generated by excess solar power. Ammonia production from nitric acid (HNO₃) may be an alternative technique for hydrogen storage. Reaction characteristics of reduction of HNO₃ using hydrogen with metal catalysts was investigated in this study.

First, the variation in NH₄⁺ production yield for metal catalysts (Al, Ni, and Cu) was investigated. It found that Cu and Ni did not contribute to ammonia production without hydrogen. Al was hydrogen generation source rather than a reduction catalyst. Ammonia production using Ni catalyst and hydrogen gas bubbles was examined at atmospheric pressure at the temperature of 60 °C. A 78.4% yield was obtained at reaction time of 4 hours. A reaction control step may be a gas exchange rate between the surface of hydrogen gas bubbles and NO₃⁻ in the solution.

KEYWORDS

Hydrogen storage, Ammonia production, HNO₃, NO_x, NH₃

INTRODUCTION

The spread of hydrogen energy has made available a strategy to control crimate change when hydrogen was produced without CO₂ emission. However, the use of hydrogen has a large energy loss due to transportation and physical storage [1, 2]. Ammonia is a hydrogen storage material that may solve several problems related to hydrogen transportation and storage [3]. Therefore, a hydrogen energy carrier and storage system using ammonia has been proposed [4]. For example, a system consisting of the hydrogen production by electrolysis of water using excess solar power, the ammonia generation using hydrogen and nitrogen, and the hydrogen generation from ammonia using catalysis decomposition, is recognized as a hydrogen storage, carrier, and utilization system. In the solar power generation site, the efficient ammonia synthesis at a low temperature and an atmospheric pressure are desired to storage hydrogen generated by excess solar power. Electrosynthesis of ammonia under atmospheric pressure is a suitable technique for the solar power generation site [5, 6], however, the efficiency of ammonia synthesis is currently insufficiency for practical use.

Ammonia production from nitric acid (HNO₃) may be an alternative technique for hydrogen storage. HNO₃ is easily produced from NO_x in flue gas from combustors by photochemical oxidation [7]. These results have created a new hydrogen energy storage, carrier, and utilization system consisting of the HNO₃ production reactor, the NH₃ production reactor, and the H₂ production reactor as shown in **Figure 1**. In this system, there are two ways to produce ammonia: direct reduction of HNO₃ using catalysts and reduction of HNO₃ using catalysts and hydrogen gas generated by solar power.

In this paper, the reaction characteristics of the ammonia production from HNO₃ at atmospheric pressure and low temperatures were examined. First, the ammonia production by direct reduction

of HNO_3 using metal catalysts was studied to use HNO_3 converted from NO_x . Second, ammonia production from HNO_3 using metal catalysts and hydrogen was investigated to store hydrogen generated from excess solar power.

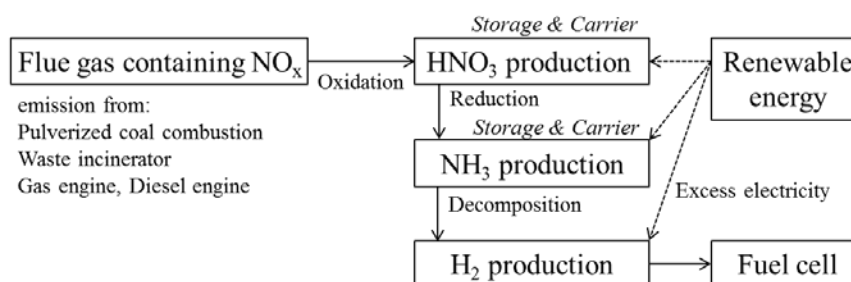


Figure 1. A proposal of new hydrogen storage, carrier, and utilization system

EXPERIMENTAL APPARATUS AND METHOD

Ammonia production by direct reduction of HNO_3

The experimental apparatus is shown in **Figure 2**. **Table 1** lists detailed reaction conditions. 450 mL of distillation water was put in the reactor, and then 2000 ppm NO_3^- solution was prepared by addition of 1.59 mL of nitric acid. 1M potassium hydroxide was added to the raw solution to adjust to $\text{pH} = 8$ or 12. Three kind of metals (Cu, Ni, and Al) as catalysts were prepared for direct reduction of NO_3^- . 3.0 g of metal catalysts were added to the test solution adjusting pH, after then the test solution was heated up to 100°C by a hot stirrer. Maximum reaction time was 4.0 h. The sampling of the solution was intermittently performed, and the concentration of NH_4^+ and NO_3^- in the solution was measured by ion chromatography.

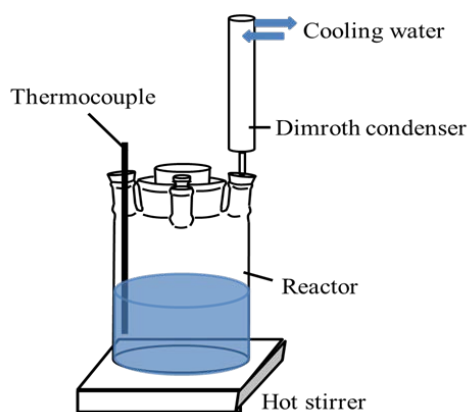


Figure 2. Experimental apparatus for direct reduction of HNO_3 using metal catalysts

Table 1. Experimental conditions in direct reduction tests

NO_3^- concentration [ppm]	2000
HNO_3 addition [mL]	1.59
KOH addition [mL]	11, 22
Reaction temperature [$^\circ\text{C}$]	100
Reaction time [h]	0.0–4.0
Solution volume [mL]	500
Metal catalyst [g]	3.0

Ammonia production from HNO₃ using hydrogen and metal catalysts

In these experiments, both metal catalysts and hydrogen gas were used to produce ammonia from HNO₃. The experimental apparatus diagram is shown in **Figure 3**. 400 mL of distilled water was put in the reactor, and 159 μL of nitric acid and 1.7 mL potassium hydroxide (1M) was added. Nitric acid ion concentration in the test solution was 200 ppm. Ni catalyst (1 g) was added to the test solution and pure hydrogen gas was fed at the flow rate of 0.5 L/min. Reaction time was 5.0 h at the temperature of 60 °C. Excess hydrogen gas was exhausted through boric acid trap. **Table 2** lists the detailed reaction condition in this experiment. The intermittently sampling of the solution was carried out, and the concentration of NH₄⁺ and NO₃⁻ was determined by ion chromatography analysis.

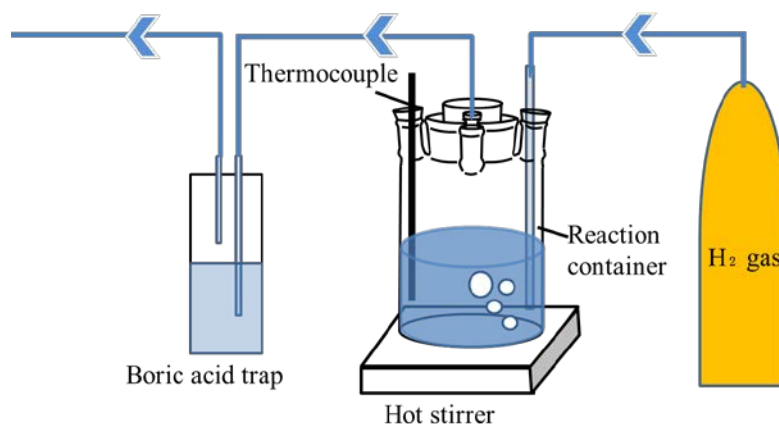


Figure 3. Experimental apparatus using metal catalysts and hydrogen gas.

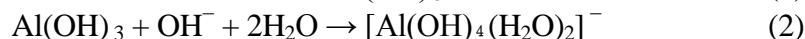
Table 2. Experimental conditions for reduction using metal catalysts and hydrogen gas

NO ₃ ⁻ concentration [ppm]	200
HNO ₃ addition [μL]	159
KOH addition [mL]	1.7
Reaction temperature [°C]	60
Reaction time [h]	0.0–5.0
Solution volume [mL]	500
Metal catalyst [g]	1.0
Hydrogen flow rate [L/min]	0.5

RESULTS AND DISCUSSION

Ammonia production by direct reduction of HNO₃

Effect of single metal catalyst (Al, Cu, and Ni) on NH₄⁺ production yield was investigated to consider direct reduction characteristics of HNO₃. **Figure 4** shows the variation in NH₄⁺ production yield based on a NO₃⁻ concentration for each catalyst. It found that Al has impacted the yield, while Cu and Ni did not contribute anything to ammonia production. NH₄⁺ production yield of 14.4% was obtained by Al addition at the reaction time of 1.0 h. Effect of Al addition on ammonia production is explained as follows:



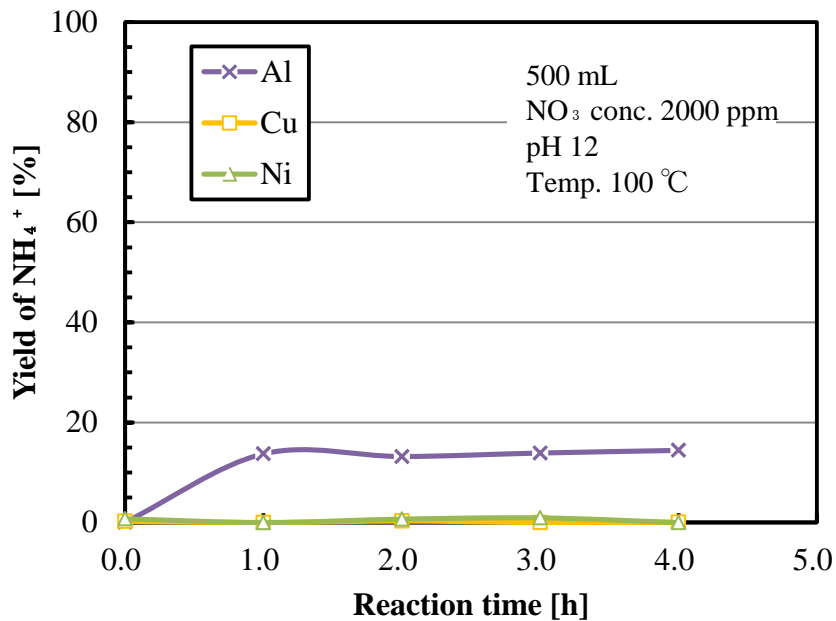
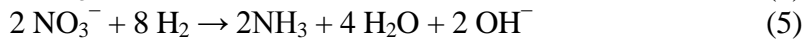
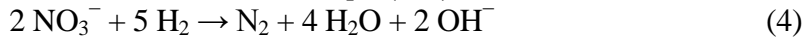
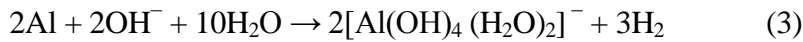


Figure 4. Effect of each metal on ammonia production for direct reduction of HNO₃

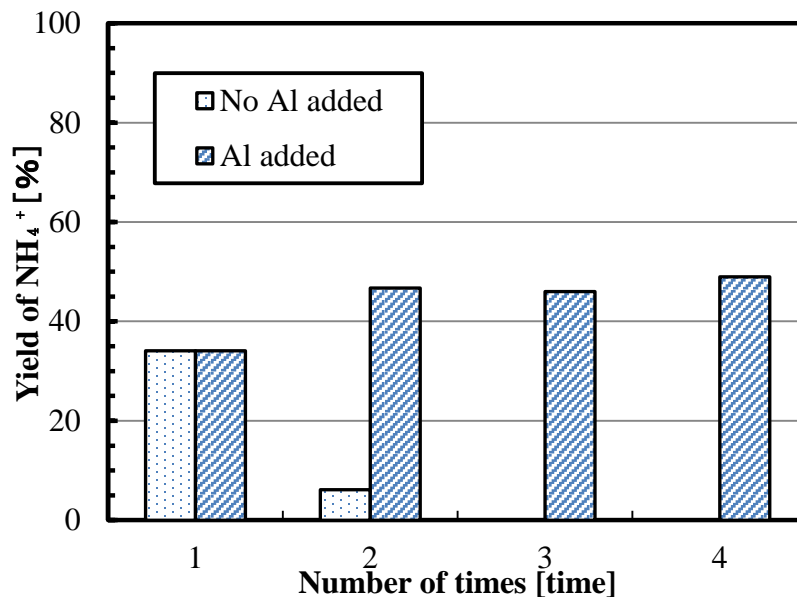


Figure 5. Variation in the NH₄⁺ yield due to aluminum consumption by repetition tests

A role of aluminum (Al) may be to supply hydrogen that is necessary for reduction of NO₃⁻ as given by reactions (1)–(3). Ammonia is generated from NO₃⁻ by hydrogen supply as given by reaction (5). In this assumption, the amount of aluminum is decreased with reaction time. Therefore, the repetition tests were carried out to be clear the role of aluminum. **Figure 5** shows variation in the yield of ammonium ion in repetition tests. In 2nd tests, the yield of NH₄⁺ was a marked decrease. On the other hand, the yield was suddenly increased in all repetition tests by addition of aluminum. Consequently, Al is hydrogen supply source rather than a reduction catalyst.

Cu and/or Ni can be expected a role of the reduction catalyst, therefore, effect of combination metals such as Cu with Al and Ni with Al were examined. Three types of the combination metal were prepared: Ni + Al, Cu + Al, and Ni + Cu + Al. **Figure 6** show the variation in NH_4^+ production yield for each combination metals.

It found that Ni + Cu + Al was the most effective combination metal because of the synergistic catalytic effect of Ni and Cu. The maximum yield of ammonium ion was 43.8% at reaction time of 2.0 h. Both Ni + Al and Cu + Al were the same characteristics as shown in Figure 6, therefore, it found that Ni and Cu have the same catalytic effect on reduction of NO_3^- . Difference in the yield of ammonium ion between combination metals and Al only is reduction effectiveness for each combination metal on reduction of NO_3^- .

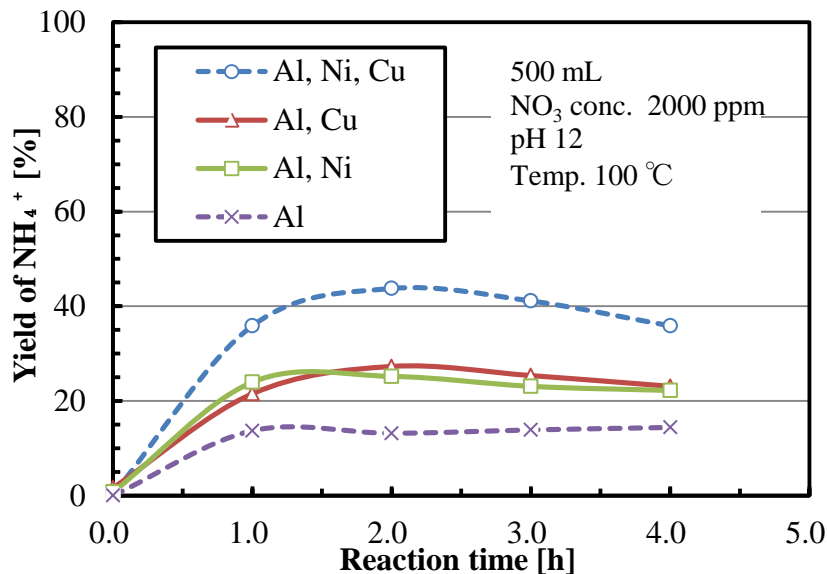


Figure 6. Variation in yield of ammonium ion for the combination of Cu, Ni, and Al.

The reduction by the combination metal catalysts may be influenced by pH of the test solution. **Figure 7** shows effect of pH on the yield of ammonium ion using the Al + Ni + Cu combination metal. The yield was higher the solution of pH = 12 than that of pH = 8. This result may be caused the amount of hydrogen generation by Al in reactions (1)–(3).

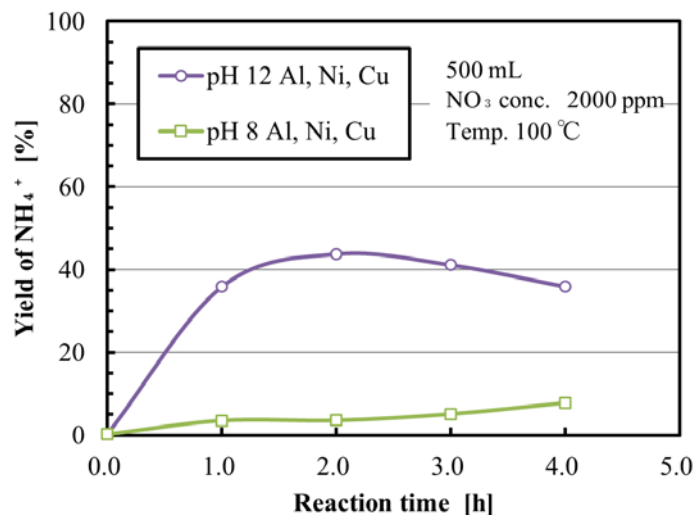


Figure 7. Effect of pH of the solution on ammonia production under Ni+Cu+Al condition

Ammonia production using Ni catalyst and hydrogen gas

The metal catalysts (Ni and/or Cu) and hydrogen as a proton supply are effective materials for ammonia production from HNO_3 at an atmospheric pressure and low temperatures. For effective storage of hydrogen generated by solar power, it is important to investigate characteristics of ammonia production using metal catalysts and hydrogen gas.

Variation in the yield of NH_4^+ was examined using the experiment apparatus shown in Figure 2. Ni catalyst (1 g) and hydrogen gas (0.5 L/min) was used for reduction of HNO_3 . As shown in **Figure 8**, a 78.4% conversion was obtained at reaction time of 4 hours. This result is a high efficiency comparing with electrosynthesis of ammonia, however, it is necessary long reaction time. In these gas-liquid reactions, a reaction control step may be a gas exchange rate between the surface of hydrogen gas bubbles and NO_3^- in liquid. The reaction time may be reduced by using micro bubbles of hydrogen gas, because a gas exchange rate is increased by the micro bubbles.

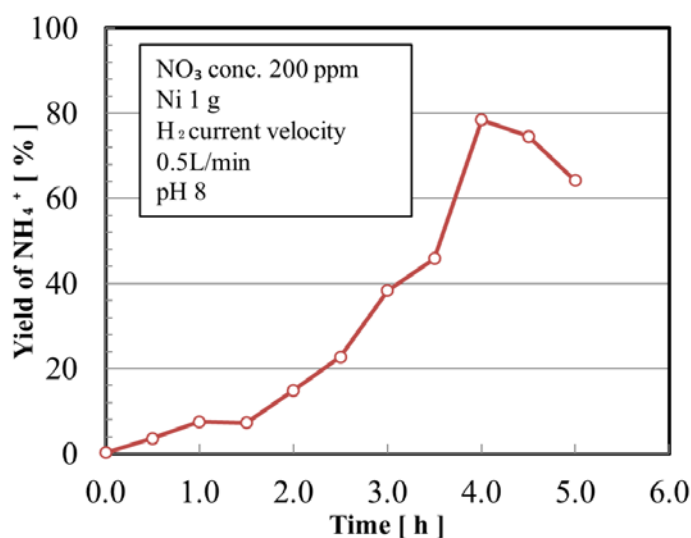


Figure 8. Ammonia production using Ni catalyst and hydrogen gas at 60 °C.

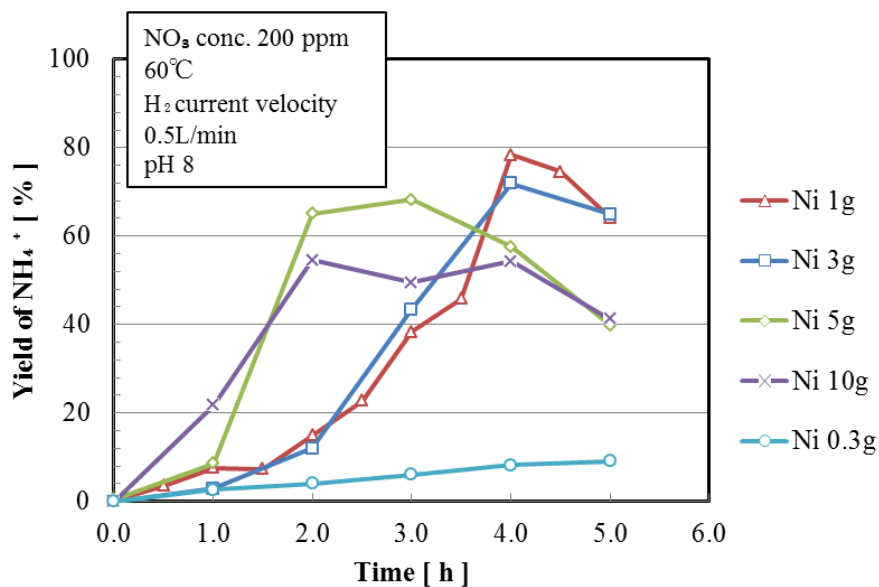


Figure 9. Effect of the amount of Ni catalyst on the yield

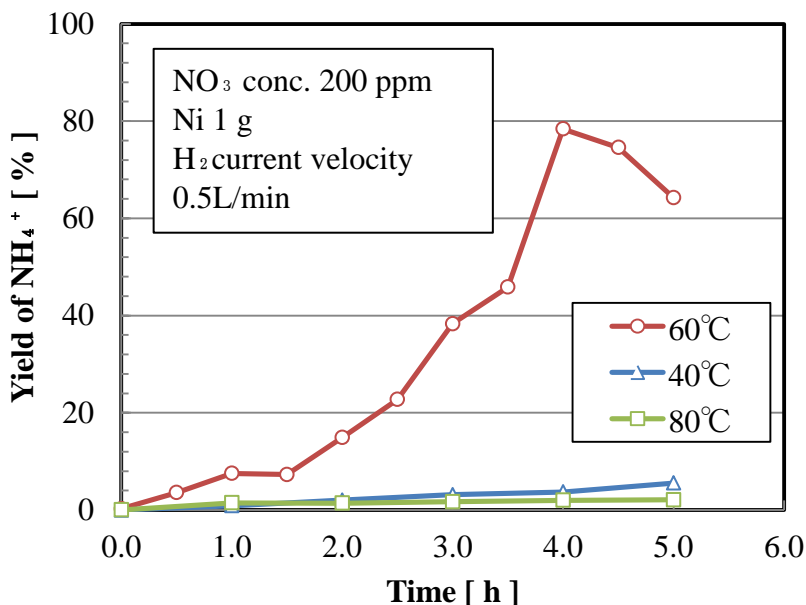


Figure 10. Effect of reaction temperatures on the yield

Figure 9 shows effect of the amount of Ni catalyst on the yield. An increase in the amount of Ni catalyst affects reaction time, while the yield was not increased though a role of Ni catalyst is reduction of NO_3^- shown in reaction (5). This is because that enough hydrogen for reduction of NO_3^- was not supplied from hydrogen bubbles.

The results of experiments varying the reaction temperature are shown in **Figure 10**. It found that the optimum temperature for the reaction was 60 °C. Temperature ammonia yield has dropped greatly when the temperature changed to 40 or 80 °C.

CONCLUSION

First, the ammonia production by direct reduction of HNO_3 using metal catalysts was studied to use HNO_3 converted from NO_x in flue gas. The role of Al, Ni, and Cu was cleared. In the direct reduction of HNO_3 , Al is necessary to supply hydrogen for reduction. Ni and/or Cu contributed to reduction of HNO_3 as catalysts. A multiple metal, Ni + Cu + Al, had the most effective catalyst for direct reduction of HNO_3 . The maximum yield of ammonium ion was 43.8% at reaction time of 2.0 h.

Second, ammonia production from HNO_3 using metal catalysts and hydrogen was investigated to store hydrogen generated from excess solar power. Simple experiments using Ni catalyst and hydrogen gas were examined. High yield of ammonia production, 78.4%, was obtained, however, reaction time of 4 hours was necessary. In this reaction, a reaction control step may be a gas exchange rate between the surface of hydrogen gas bubbles and NO_3^- in liquid, which has to improve for reduction of the reaction time. Effect of the amount of Ni catalyst and reaction temperatures was also investigated. The optimum reaction temperature was 60 °C. An increase in the amount of Ni catalyst was decreased the reaction time.

ACKNOWLEDGMENT

The authors would like to acknowledge that the funding for this study was provided by JST (A-STEP).

REFERENCES

1. Eberle U, Felderhoff M, Schueth F., Chemical and physical solutions for hydrogen storage, *Angew Chem. Int. Edit.*, Vol.48, 6608–6630, 2009.
2. Lan, R, Irvine, J. T. S. and Tao, S., Ammonia and Related Chemicals as Potential Indirect Hydrogen Storage Materials, *Int. J. Hydrogen Energy*, Vol. 37, No. 2, pp 1482-1494, 2012.
3. Green Jr L., An ammonia energy vector for the hydrogen economy, *Int. J. Hydrogen Energy*, Vol.35, 355–359, 1982.
4. Kojima Y., *J. Jpn. Inst. Energy*, Vol.93 No.5, pp.378–385, 2014. (in Japanese)
5. Pickett C.J., Talarmin J., Electrosynthesis of ammonia, *Nature*, Vol.317, 652–653, 1985.
6. Skodra A., Stoukides M., Electrocatalytic synthesis of ammonia from steam and nitrogen at atmospheric pressure, *Solid State Ionics*, Vol.180, 1332–1336, 2009.
7. M. Watanabe, S. Kambara Hydrogen energy storage system originated from nitrogen oxides in flue gas, *Proceedings of the 10th Conference on Sustainable Development of Energy, Water and Environment Systems*, SDEWES2015.1054, 6 pages, Dubrobnik (Croatia), 2015.
8. N. Wehbe, M. Jaafar, C. Guillard, J.-M. Herrmann, S. Miachon, E. Puzenat, N. Guihaume, Comparative study of photocatalytic and non-photocatalytic reduction of nitrates in water, *Applied Catalysis A: General*, 368, pp.1-8, 2009.