

Ammonia production from nitric acid for hydrogen carrier system

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Abstract

An original energy carrier system has been developed, which is consisted of a reactor of HNO₃ production from NO_x in flue gas generated from combustors, an NH₃ production reactor by reduction of HNO₃, and a H₂ production device from NH₃. NH₃ is a key material as a hydrogen carrier and storage in the system. The objective of this study is to develop an effective reaction method of ammonia production from HNO₃. Diluted HNO₃ solution was mixed with Al as the proton source, Cu, and Ni as a catalyst for reduction, and then pH was adjusted into 12 by potassium nitrate solution. The reduction was carried out at solution temperature of 100 °C. In this reaction method, ammonia yield was attained approximately 40%. And more, a difference reaction method has been tried to reduce production cost, which was to find alternative source of Al; it is using Ni catalyst and hydrogen gas. In this system, the maximum NH₄⁺ yield was approximately 80%.

1. 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, an 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 Fig. 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

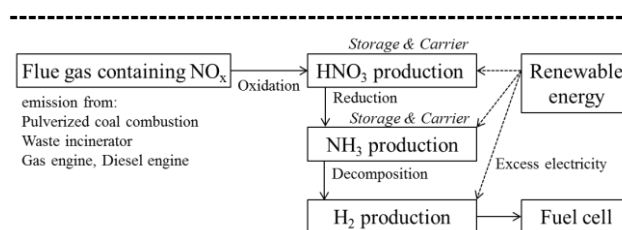


Fig. 1. A proposal of new hydrogen storage, carrier, and utilization system.

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.

2. Experimental apparatus and method

2.1 Ammonia production by direct reduction of HNO_3 .

The experimental apparatus is shown in Fig. 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 for adjusting the pH, which was adjusted 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.

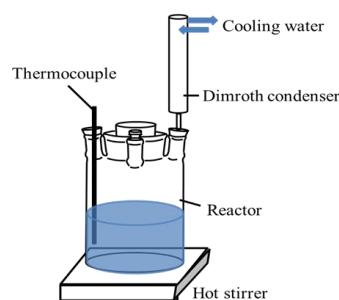


Fig. 2. Experimental apparatus for direct reduction of HNO_3 using metal catalysts

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 [°C]	100
Reaction time [h]	0.0 - 4.0
Solution volume [mL]	500
Metal catalyst [g]	3.0

2.2 Ammonia production from HNO_3 using hydrogen and metal catalysts

In this experiments, both metal catalysts and hydrogen gas were used to produce ammonia from HNO_3 .

The experimental apparatus diagram is shown in Fig. 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.

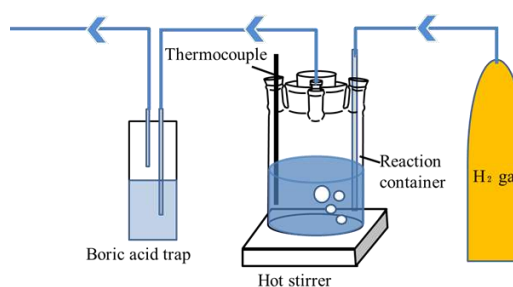


Fig. 3. Experimental apparatus using metal catalysts and hydrogen gas.

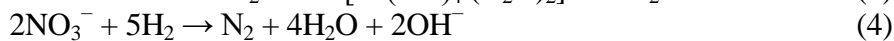
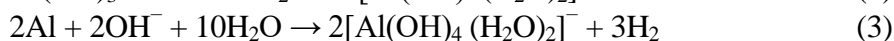
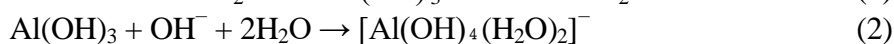
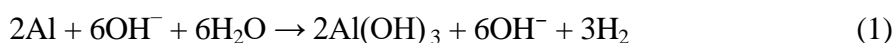
Ni catalyst (1 g) was added to the test solution and pure hydrogen gas was fed at the flow rate of 0.5 L/min. Reaction time was 5.0 h at the temperature of 60 °C. Excess hydrogen gas was exhausted through boric acid trap. Table 2 lists the detailed reaction condition in this experiment. The intermittently

sampling of the solution was carried out, and the concentration of NH_4^+ and NO_3^- was determined by ion chromatography analysis.

3. Results and discussion

3.1 Ammonia production by direct reduction of HNO_3

Effect of single metal catalyst (Al, Cu, Ni) on NH_4^+ production yield was investigated to consider direct reduction characteristics of HNO_3 . Fig. 4 shows the variation in NH_4^+ production yield based on a NO_3^- concentration for each catalyst. It found that Al has impacted the yield, while Cu and Ni did not contribute anything to ammonia production. NH_4^+ 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:



A role of aluminum (Al) may be to supply hydrogen that is necessary for reduction of NO_3^- as given by reactions (1)–(3). Ammonia is generated from NO_3^- 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. Fig.5 shows variation in the yield of ammonium ion in repetition tests. In 2nd tests, the yield of NH_4^+ was a marked decrease. On the other hand, the yield was suddenly increased in all repetition tests by addition of aluminum. Consequently,

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

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

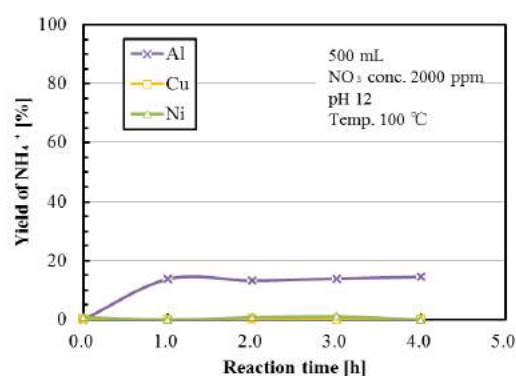


Fig. 4. Experimental apparatus using metal catalysts and hydrogen gas.

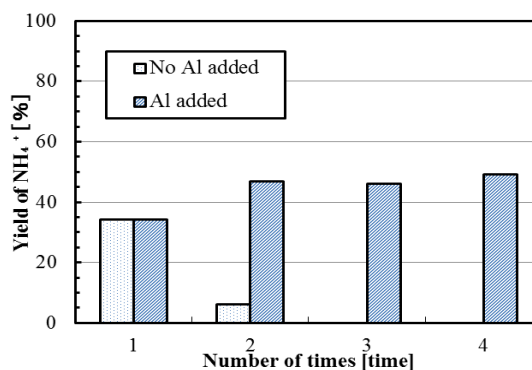


Fig. 5. Experimental apparatus using metal catalysts and hydrogen gas.

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. Fig. 6 shows 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^- .

The reduction by the combination metal catalysts may be influenced by pH of the test solution. Fig. 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).

3.2 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 Fig. 8, a 78.4% conversion was

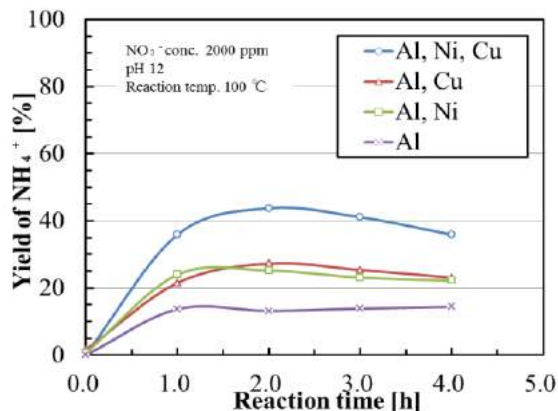


Fig. 6. Experimental apparatus using metal catalysts and hydrogen gas.

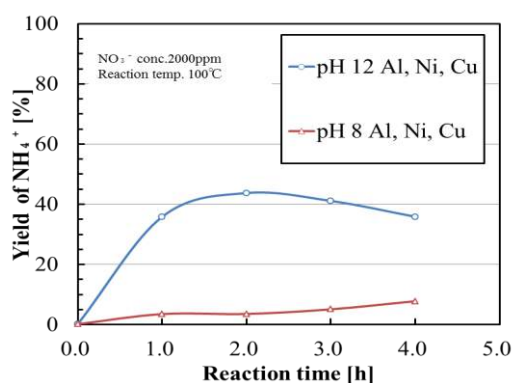


Fig. 7. Experimental apparatus using metal catalysts and hydrogen gas.

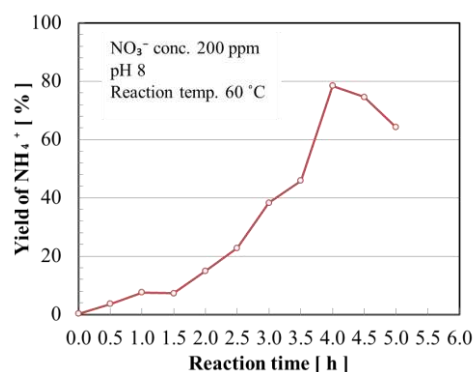


Fig. 8 Experimental apparatus using metal catalysts and hydrogen gas.

obtained at reaction time of 4 hours. This result is a high efficiency comparing with electro synthesis of ammonia, however, it is necessary long reaction time.

Fig. 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 Fig. 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.

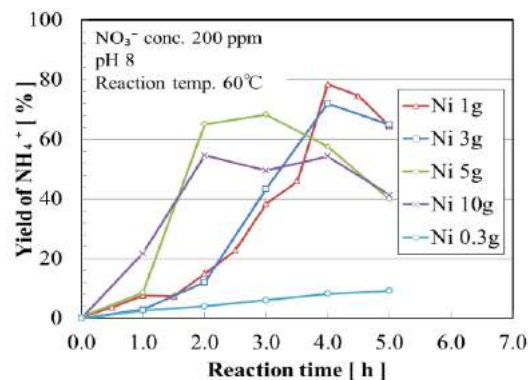


Fig. 9 Experimental apparatus using metal catalysts and hydrogen gas.

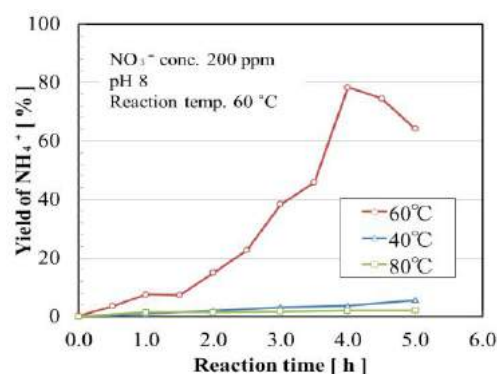


Fig. 10. Experimental apparatus using metal catalysts and hydrogen gas.

Conclusions

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. Effect of the amount of Ni catalyst and reaction temperatures were also investigated. The optimum reaction temperature was 60 °C. An increase in the amount of Ni catalyst was decreased the reaction time.

Acknowledgements

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