Hydrogen energy storage system originated from nitrogen oxides in flue gas

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ABSTRACT

An innovative energy storage and carrier system has proposed from our recent researches. The system has three kind of chemical reactors, which are a HNO_3 production reactor, a NH_3 production reactor, and a H_2 production reactor. In this paper, we focused on characteristics of HNO_3 production originated from nitrogen oxides in flue gas. HNO_3 was produced by photochemical oxidation of nitric oxide (NO_x) using vacuum ultraviolet irradiation of 172 nm wavelength. The HNO_3 production was affected by the flow rates of the model flue gas. It found that a high NO removal rate was obtained in the $NO/O_2/H_2O/N_2$ system. A maximum NO conversion to HNO_3 was 97.4%. The effect of the gap length on the reaction rate constant k on the NO conversion to enhance the HNO_3 production. The k was 0.193 s^{-1} for the ϕ80 reactor, whereas the k increased to 0.658 s^{-1} for the ϕ60 reactor.

KEYWORDS

Hydrogen, Ammonia, NO_x, HNO_3, Vacuum ultraviolet, Storage, Energy carrier

INTRODUCTION

The introduction of a hydrogen economy has been an available strategy to control criminate change when hydrogen is produced without CO_2 emission. However, use of hydrogen has a large energy loss for its transportation and physical storages [1, 2]. Ammonia is a hydrogen storage material that may solve several problems related to the hydrogen transportation and storage in a hydrogen economy [3]. Therefore, an energy carrier and storage system using ammonia has been proposed [4]. For example, a system consisting of the hydrogen production by electrolysis of water, ammonia synthesis from hydrogen, and the hydrogen generation from ammonia, is recognized as a hydrogen carrier and storage system without CO_2 emission. However, the efficiently ammonia synthesis is currently difficult, though some researches have been performed ammonia synthesis studies at a low temperature and pressure [5, 6].

We have been developed an original deNO_x reactor using vacuum ultra violet (VUV) of 172 nm wavelength [7]. Recently, we found that nitric acid (HNO_3) was easily produced from NO_x by photochemical oxidation. HNO_3 is an available material for NH_3 production, because NH_3 can generate from HNO_3 by reduction at atmosphere pressure and a low temperature [8]. On the other hand, an original plasma membrane reactor for H_2 production from ammonia also has been developed [9]. Using the plasma membrane reactor, pure hydrogen production for fuel cells was attained the flow rate of 21 L/h. These results have created a new hydrogen energy storage and carrier system consisting of the HNO_3 production reactor, the NH_3 production reactor, and the H_2 production reactor as shown in **Figure 1**. The advantage of this system is to combine deNO_x without ammonia. Selective catalytic reduction (SCR) has been usually used for various combustors to remove NO_x, which needs catalysts and ammonia for deNO_x. If the energy system

shown in Figure 1 installs to the combustors, the cost of catalyst and ammonia would be reduced. Furthermore, excess electricity of renewable energy can use to drive each reactor; therefore hydrogen may be able to inexpensively produce. It is important for the establishment of this system to achieve high energy efficiency in each reactor.

In this paper, we focused on characteristics of HNO_3 production. The present study aimed to investigate fundamental characteristics of the HNO_3 production using the photochemical reactor. The effects of the flow rates and the chemical composition on HNO_3 production using VUV was examined. Furthermore the effect of the gap length in the reactor on the NO conversion to HNO_3 for an enhancement of the HNO_3 production.

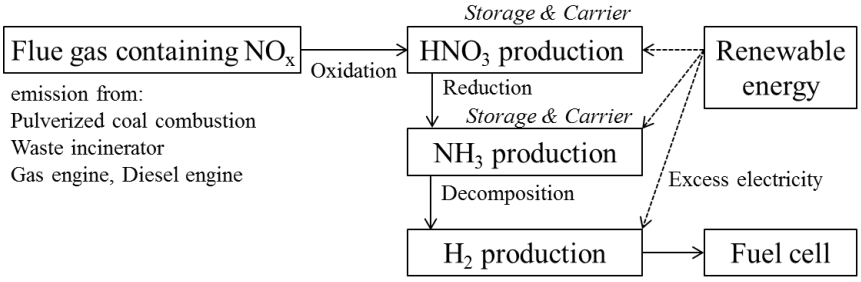

Figure 1. A proposal of a new hydrogen energy storage and carrier system

EXPERIMENTAL APPARATUS AND METHOD

The experimental setup is shown in **Figure 2**. The apparatus consists of the gas mixing and flow control systems, the humidifier, the photochemical reactor, and the gas analysers. In experiments for HNO_3 production, an N_2/Air gas mixture was prepared using the mass-flow controllers (MFCs) and the gas blender, and after then, moisture and NO gas were mixed. The $NO/O_2/H_2O/N_2$ gas mixture was fed into the photochemical reactor as the model flue gas. The gas temperature depended on a H_2O concentration in the humidifier, which was varied from 30 °C to 60 °C. The temperature of a gas feed pipe maintained above the temperature of the humidifier by a line heater because of prevention of H_2O condensation in the pipe.

The photochemical reactor (inner diameter: 80 mm) was had a coaxial configuration with the excimer lamp (outer diameter: 40 mm; USHIO Inc.). A dielectric-barrier discharge (DBD) plasma unit using xenon gas was installed as part of the excimer lamp. When a high voltage was applied to an electrode of the DBD by the AC power source, Xe atoms were excited by the electron energy from the DBD plasma, and excited Xe atoms were returned instantaneously to their ground states. In this process, a narrow wavelength distribution having a peak intensity at 172 nm was continuously emitted. The model flue gas was fed into the gap between the excimer lamp and the inside wall of the cylindrical reactor. The gap volume was 377 cm^3. The radiation power was 26 $mW \cdot cm^{-2}$ on the quartz glass surface of the excimer lamp. The pressure of the reactor was controlled to be slightly above atmospheric pressure using a gas sampler (SHIMAZU CFP-8000), which featured suction pumps and gas coolers. The gas composition of the output stream was continuously measured by gas analysers for NO, NO_2 (HORIBA VIA510), O_2 (SHIMAZU NOA-7000), and N_2O (HORIBA VIA510).

Table 1 details the experimental conditions for HNO_3 production. The total flow rate of the model flue gas was varied from 1.0 to 5.0 L min^{-1}, and a NO concentration in the model gas was fixed 1500 ppm on dry basis. The O_2 concentration and the H_2O partial pressure as saturated vapour pressure were changed as listed in Table 1.

The temperature of the model gas was heated to approximately 150 °C in the photochemical reactor by radiation of joule heating from the excimer lamp surface; moisture in the gas did not

condensed on the wall of the reactor. The power consumption of the excimer lamp at the plug was 90 W.

In all experimental conditions, the concentration of HNO_3 produced by the photochemical reaction was determined. The produced gas was introduced to the absorbing solution by switching the valves, and HNO_3 was completely recovered. The concentration of nitrate ion (NO_3^-) in the solution was measured by the ion analyser (Toa-DKK IA-300).

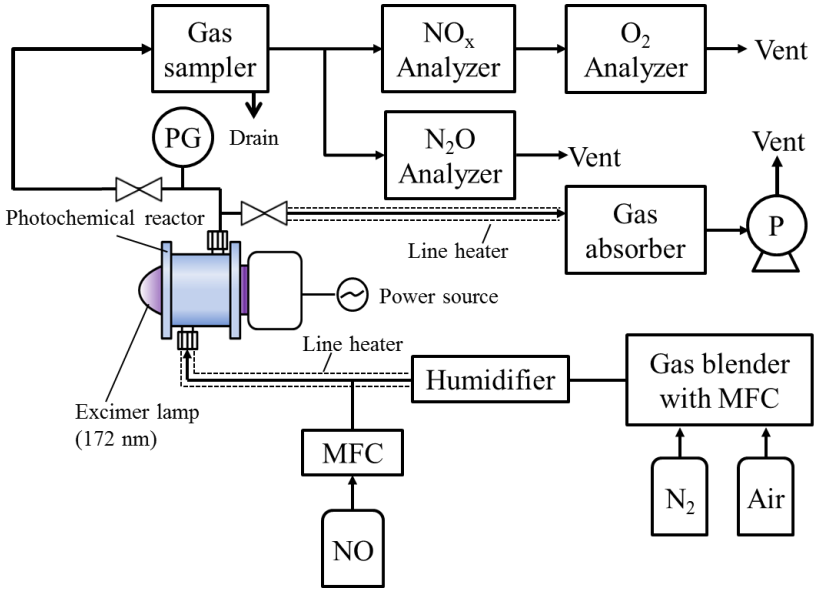

Figure 2 Experimental setup for HNO_3 production using VUV of 172 nm wavelength

Table 1 Experimental conditions for HNO_3 production

Total flow rate of model gas [L/min]	1.0–5.0
NO concentration [ppm,dry]	1500
O_2 concentration [%, dry]	0, 8.3
H_2O partial pressure [kPa]	0–9.5

RESULTS AND DISCUSSION

Fundamental characteristics of HNO_3 production

Figure 3 shows the effect of the flow rates of the $NO/O_2/H_2O/N_2$ gas mixture on the NO conversion to HNO_3. The NO conversion to HNO_3 was calculated from the NO removal rate as follows:

$$\text{NO removal rate [\%]} = ([NO]_{IN} - [NO_x]_{OUT})/[NO]_{IN} \times 100 \quad (1)$$

$$\text{NO conversion to } HNO_3 \text{ [\%]} = \text{NO removal rate [\%]} \quad (2)$$

where $[NO]_{IN}$ is the initial NO concentration (1500 ppm by volume) and $[NO_x]_{OUT}$ is the total concentration of NO, NO_2, N_2O (ppm, dry) in the gas produced by the photochemical reactor. However, in the $NO/O_2/H_2O/N_2$ gas mixture experiments, NO_2 and N_2O was not detected. Furthermore the output mass of N was agreed with that of the input mass; therefore, Eq.2 is correct in the $NO/O_2/H_2O/N_2$ gas mixture experiments.

The NO conversion to HNO_3 was attained 97.4% at the flow rate of 1.0 L min^{-1}, while it was decreased with an increase in the flow rate of the $NO/O_2/H_2O/N_2$ gas mixture. The each chemical

composition absorbs the light of 172 nm wavelength [10], and occurs various reactions. For example, the below reactions may concern:

$$H_2O + h\nu \rightarrow OH + O \quad (3)$$
$$O_2 + h\nu \rightarrow O + O \quad (4)$$
$$NO + OH + O \rightarrow HNO_3 \quad (5)$$

where h is Planck constant, and ν is frequency which is given by c/λ (c is the speed of light, and λ is wavelength).

In general, the reaction rate in the gas phase reaction such as Eq. (5) depends on the reaction time or gas residence time in the reactor. Therefore, the NO conversion to HNO_3 was affected by the flow rates.

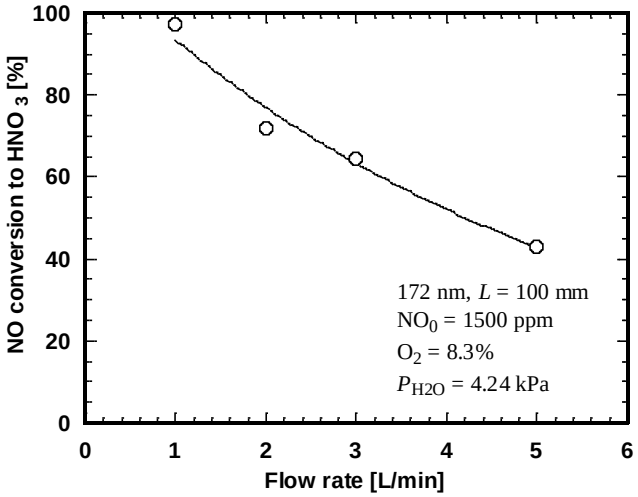

Figure 3. Variation in NO conversion rate to HNO_3 with flow rate of the model gas

・Reaction paths of HNO_3 production

To find effective reaction paths of the HNO_3 production, the four systems were examined as follows:

1) NO/N_2
2) $NO/H_2O/N_2$
3) $NO/O_2/N_2$
4) $NO/O_2/H_2O/N_2$

Figure 4 shows the effect of gas composition on the NO removal rate as a function of the partial pressure of H_2O. It found that high NO removal rate was obtained at the $NO/O_2/H_2O/N_2$ system only. Both O_2 and H_2O were necessary for a high NO conversion to HNO_3. In particular, the partial pressure of H_2O was needed above 4.24 kPa for efficiency HNO_3 production in the experimental conditions.

In the $NO/O_2/H_2O/N_2$ system, the reactions relating to the HNO_3 production were considered as follows:

$$O_2 + O \rightarrow O_3 \quad (6)$$
$$NO + O_3 \rightarrow NO_2 + O_2 \quad (7)$$
$$NO_2 + OH \rightarrow HNO_3 \quad (8)$$

In fact, the generation of ozone was detected by qualitative analysis of ozone at the photochemical reactor exit. The issue on the enhancement of HNO_3 production is to find

rate-controlling step among Eqs.(3)–(8), but the kinetic reaction study will be conducted in future.

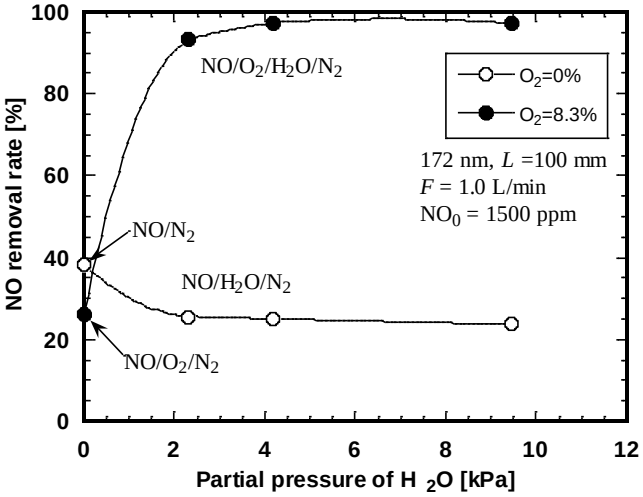

Figure 5. Effects of P_{H2O} and gas composition on NO conversion to HNO_3

・**Enhancement of HNO_3 production**

An efficiently VUV absorption of molecules is important for the enhancement of the HNO_3 production. The photon energy *hv* is attenuated toward the inner wall in the photochemical reactor; therefore the gap length (or inner diameter of the reactor) affects the NO conversion to HNO_3.

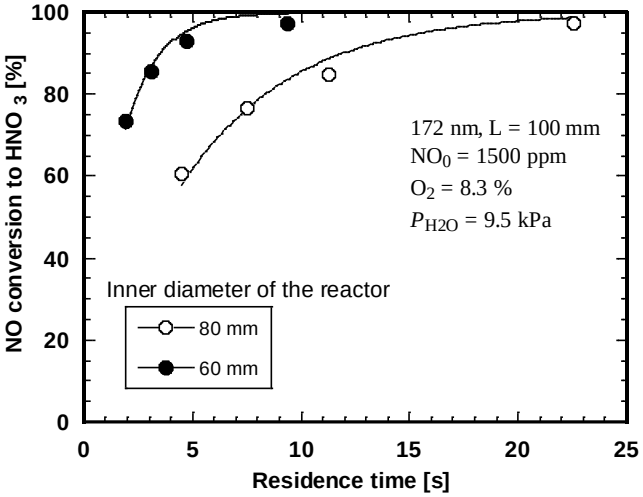

Figure 5. Effects of P_{H2O} and gas composition on NO conversion to HNO_3

To investigate the effect of the gap length, the photochemical reactor having an inner diameter of 60 mm was prepared. **Figure 5** shows variation in the NO conversion to HNO_3 with an increase in gas residence time as a parameter of the inner diameter of the reactor. The gap length of the ϕ60 reactor and the ϕ80 reactor was 10 and 20 mm, respectively. The NO conversion to HNO_3 enhanced using the photochemical reactor having the narrow gap length, even though gas residence time was short. This is because that molecular H_2O and O_2 were effectively absorbed the VUV of the 172 nm wavelength in the narrow space.

The reaction rate of the HNO_3 production assumes first-order reaction:

$$dX/dt = k\,X \quad (9)$$

$$X = 100 \times (1 - \exp(-k\,t)) \quad (10)$$

where X is NO convesion to HNO_3 [%], t is gas residence time [s], and k is rate constant [s^{-1}].

The solid line in Figure 5 is the fitting line by Eq.(10). The k was 0.193 s^{-1} for the ϕ80 reactor, whereas the k was 0.658 s^{-1} for the ϕ60 reactor. The k was enhanced 3.4 times in the narrow gap length.

CONCLUSION

A new hydrogen energy storage and system consisting of the HNO_3 production reactor, the NH_3 production reactor, and the H_2 production reactor has proposed from the recent research results. In this paper, the fundamental characteristics of the NO conversion to HNO_3 using photochemical reactor with vacuum ultraviolet irradiation of 172 nm wavelength.

The HNO_3 production was affected by the flow rates and the chemical composition of the model flue gas. The maximum HNO_3 production was 97.4% in the $NO/O_2/H_2O/N_2$ system. O_2 and H_2O were necessary for the HNO_3 production, and the partial pressure of H_2O was needed above 4.24 kPa for efficiently HNO_3 production.

To enhance the HNO_3 production, the effect of the gap length on the reaction rate constant k was examined. The NO conversion to HNO_3 increased using the photochemical reactor having the narrow gap length, even though gas residence time was short. The k was 0.193 s^{-1} for the ϕ80 reactor, whereas the k increased to 0.658 s^{-1} for the ϕ60 reactor.

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