CO₂ reduction using adsorption followed by nonthermal plasma treatment

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Abstract. Carbon dioxide (CO₂) is one of the main substances linked to global warming, and its emission should be reduced. In this study, a CO₂ reduction treatment using an adsorbent and a nonthermal plasma flow is investigated. This treatment comprises a physical adsorption process and nitrogen (N₂) plasma reduction process. In the physical adsorption process, CO₂ is adsorbed by the adsorbent. In the N₂ plasma reduction process, the adsorbed CO₂ is reduced to CO by a nonthermal plasma flow that is generated by a plasma reactor with a circulating N₂ plasma flow. The generated CO can be reused as a fuel. We estimate this experimental results by calculating conversion efficiency of CO₂ to CO. In the N₂ plasma reduction process, the CO concentration reaches approximately 1%, regardless of the number of experiments, and conversion efficiency reaches at most 5.3%.

1. Introduction
In recent years, global warming has become a worldwide problem. Carbon dioxide (CO₂) is one of the main substances linked to global warming, and its emission should be reduced. However, the proposed CO₂ removal technologies such as chemical adsorption technology using aqueous alkanolamine solutions require a large cost [1]. Therefore, CO₂ treatment technology having a low cost and high efficiency is required. One promising technology is the conversion of CO₂ to CO by a plasma treatment [2] because CO can be used as fuel for combustion engines.

In this study, a CO₂ reduction treatment system using an adsorbent and a nonthermal plasma flow is investigated. In this experiment, CO₂ is adsorbed by the adsorbent, then the adsorbed CO₂ is reduced to CO by a nonthermal plasma flow. We develop a highly efficient CO₂ reduction treatment system using an adsorbent and a nonthermal plasma flow at the laboratory scale.

2. Experimental setup and method
A schematic diagram of the experimental apparatus is shown in figure 1. In the physical adsorption process, valves F, H, I, and J are opened. An adsorbent with a volume of 1.22 L is placed in the adsorbent chamber that is downstream from the plasma reactor. As an adsorbent, the molecular sieve zeolite 13X (APG-III) [3] is used. CO₂ gas at a concentration of 10.0% with a flow rate of 10 L/min is prepared by a 99.5% CO₂ cylinder and an air cylinder, then introduced into the experimental apparatus, and exhausted through valve H. In this process, CO₂ is adsorbed by the adsorbent. The upstream and downstream CO₂ concentrations from the adsorbent chamber are measured with a gas-detecting tube every 10 min. When adsorption is completed, measurement is finished. It is known that adsorption is
completed when the upstream and downstream CO$_2$ concentrations reach a steady state. After the physical adsorption process, the flow channel in the apparatus is purged with N$_2$. First, only valves C, D, E, and H are opened, and 99.5% N$_2$ gas with a flow rate of 10 L/min is prepared by a 99.5% N$_2$ cylinder. Then, N$_2$ is introduced into the experimental apparatus by opening valve L for 60 min. After that, only valves E, G, and H are opened. Then, 99.5% N$_2$ gas is introduced into the experimental apparatus by opening valve L for 10 min. The O$_2$ concentration in the flow channel is measured with an O$_2$ analyzer. When the N$_2$ purge is completed, the O$_2$ concentration in the flow channel becomes less than 1.0%.

In the N$_2$ plasma reduction process, the circulation flow channel is set by opening valve C, D and G, and the N$_2$ plasma flow is then generated by a plasma reactor and a blower with a flow rate of 0.54 m$^3$/min. Owing to the N$_2$ plasma flow, the CO$_2$ adsorbed by the adsorbent is desorbed and reduced to CO with plasma chemical reactions shown in reference [2]. The CO, CO$_2$, and O$_3$ concentrations are measured at a tank with a gas-detecting tube every 10 min. O$_3$ concentration is also measured every 10
After the discharge is finished, only valves C, D, E, H, and K are opened; then, the gas in the flow channel is discharged to the air through a MnO$_2$ catalyst by a blower.

In both the physical adsorption process and N$_2$ plasma process, the temperatures of the adsorbent and upstream temperatures of the plasma reactor are measured by thermocouples every 30 s. Upstream temperatures of the plasma reactor in the adsorption and reduction processes are approximately 25°C and 40°C, respectively.

Figures 2 and 3 show a schematic diagram of the plasma reactor (90 mm × 425 mm × 100 mm) and a discharge element, respectively. The plasma reactor consists of twelve surface discharge elements that are energized by a 10-kHz bipolar pulsed high-voltage power supply. The power consumption is 300 W, and the electrodes face toward upstream gas.

The conversion efficiency of CO$_2$ to CO ($\eta_{CO}$) is defined as

\[
\eta_{CO} = \frac{V_{CO}}{V_{adsCO2} + V_{CO2}} \times 100
\]

where $V_{CO}$ and $V_{CO2}$ are the volume of the CO generation and initial volume of CO$_2$ in the N$_2$ plasma reduction process, respectively. $V_{adsCO2}$ is the volume of the adsorbed CO$_2$ in the adsorption process.

### 3. Experimental results and discussion

Figure 4 shows the CO$_2$ concentrations as a function of the treatment time in the physical adsorption process. It is observed in figure 4 that the upstream concentration is stable at approximately 9.5% until 120 min from 10 min. On the other hand, the downstream concentration increases monotonically until 70 min from the start of treatment and is stable at 8.0% after that time. Therefore, the absorbent is almost saturated at 70 min. The volume of adsorbed CO$_2$ is 32.6 L during the process. The temperature in the adsorbent chamber increases rapidly until 20 min and decreases slowly after that time. Therefore, CO$_2$ is actively adsorbed until 20 min from the start of treatment.

Figure 5 shows the CO, CO$_2$, and O$_2$ concentrations as a function of the treatment time for the N$_2$ plasma reduction process. The CO concentration reaches approximately 1% at 70 min and is stable after that time. The CO$_2$ concentration increases monotonically until 30 min from the start of treatment and is stable at 4.0% after that time. The O$_2$ concentration increases monotonically. Therefore, the treatment time of 70 min is the suitable condition in this experiment because this time is required to reduce CO$_2$ to CO at the lowest power possible. In addition, the conversion efficiency is at most 2.2% when the treatment time is 70 min. The O$_3$ concentration is less than 5 ppm during the treatment.

The results when the experiment is repeated with the same adsorbent are shown in figures 6 and 7. The number of repetitions of the experiment is four. It is observed in figure 6 that the CO$_2$ concentrations of experiments 2–4 increase more rapidly and are stable earlier than experiment 1. The volume of adsorbed CO$_2$ in experiment 1 is 32.6 L, whereas those of experiments 2, 3, and 4 are between 10 L and 20 L. This is because part of the CO$_2$ adsorbed by the adsorbent is not desorbed during the N$_2$ plasma reduction process. It is assumed that CO generation increases by increasing the amount of CO$_2$ desorbed. Therefore, it is necessary to improve CO$_2$ desorption by heating the adsorbent using waste heat from CO$_2$ emission source such as boilers and engines.

It is observed in figure 7 that the CO concentration reaches approximately 1%, regardless of the number of experiments, whereas the CO$_2$ concentration varies between 3% and 5%. The CO concentrations of experiments 2 and 4 increase with the elapsed time until the treatment is finished. The conversion efficiency reaches at most 5.3%. Therefore, it is necessary that we increase the treatment time. Furthermore, it is necessary to change other parameters such as the flow rate of the blower, the volume of adsorbent, and the temperature of the adsorbent chamber to improve CO generation and the conversion efficiency.

### 4. Conclusion

In this study, a CO$_2$ reduction treatment system using an adsorbent and a nonthermal plasma flow is investigated. A volume of CO$_2$ of 32.6 L is adsorbed by the adsorbent with a volume of 1.22 L in 120
min during the physical adsorption process. In the N\textsubscript{2} plasma reduction process, it is observed that CO\textsubscript{2} is reduced to CO. We repeat this process four times with the same adsorbent, and it is observed that the CO concentration reaches approximately 1\%, regardless of the number of experiments. The conversion efficiency reaches at most 5.3\%. When the treatment is finished, The CO concentrations of experiments 2 and 4 increase with the elapsed time until the treatment is finished. Therefore, it is necessary to increase the treatment time, and change other parameters such as the flow rate of the blower, the volume of the adsorbent, and the temperature of the adsorbent chamber to improve CO generation and conversion efficiency.

**Figure 4.** CO\textsubscript{2} concentrations during the physical adsorption process.

**Figure 5.** CO\textsubscript{2}, CO, O\textsubscript{2} concentrations during the N\textsubscript{2} plasma reduction process.

**Figure 6.** CO\textsubscript{2} concentrations during the physical adsorption process. The experiment is repeated four times.

**Figure 7.** CO\textsubscript{2} concentrations during the N\textsubscript{2} plasma reduction process. The experiment is repeated four times.

**Acknowledgments**

This work is partially supported by JSPS KAKENHI, Grant Number 25630408, and a grant from the Steel Foundation for Environmental Protection Technology.

**References**

[1] Yu C-H, Huang C-H and Tan C-S 2012 Aerosol Air Quality Res. 12 745

[2] Spencer L F and Gallimore A D 2011 Plasma Chem. Plasma Process. 31 79

[3] UOP LLC, a Honeywell Company, UOP MOLSIV\textsuperscript{TM} APG-III Adsorbent, catalog, http://www.uop.com/?document=uop-apg-iii-adsorbent-brochure&download=1