

Research Paper

Study on Chemical Removal of Nitric Oxide (NO) as a Main Cause of Fine Dust (Air Pollution) and Acid Rain

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Abstract This study was conducted to remove NO_x, which is the main cause of fine dust and air pollution as well as acid rain. NO_x was tested using 3% NO (diluted in He) as a simulated gas. Experiments were sequentially carried out by oxidizing NO to NO₂ and absorbing NO₂. Especially, we focused on the changes of NO oxidation according to both oxidant (NaClO₂) concentration change (1~10 M) and oxidant pH change (pH = 1~5) by adding HCl. In addition, we tried to suggest a method to improve NO₂ absorption by conducting NO₂ reduction reaction with reducing agent (NaOH) concentration (40~60%). It was found that NO removal efficiency increased as both concentration of oxidant and flow rate of NO gas increased, and NO decreased more effectively as the pH of hydrochloric acid added to the oxidant was lower. The NO₂ adsorption was also better with increasing NaOH concentration, but the NO removal efficiency was ~20% lower than that of the selective NO reduction. Indeed, this experimental method is expected to be a new method that can be applied to the capture and removal of fine dust caused by air pollution because it is a method that can easily remove NO gas by a simple device without expensive giant equipment.

Keywords: NO oxidation, NO₂ absorption, Fine dust, Air pollution, Acid rain

I. Introduction

Fine dust that is striking our country every spring is often from China, but most of them come from cars using diesel engines [1]. If we do not solve this problem, Korea's fine dust problem will not be solved forever. However, people have not found a solution to the problem other than reducing diesel-powered vehicles, and many still do not see the problem of solving the fine dust problem. Particulate Matter (PM) or dust is an air pollutant containing a large number of air pollutants together with sulfur dioxide, nitrogen oxides, lead, ozone, carbon monoxide, etc. It occurs in automobiles, factories, etc., and it is referred to as "PM10". When the particle is 2.5 μm or less, it is referred to as "PM_{2.5}" and called as "ultrafine dust" [1]. Air pollutants from fossil fuels such as petroleum and coal or from exhaust fumes from automobile soot are known to be the main cause of fine dusts, but methods for completely removing ultrafine dusts have not been developed yet [1,2].

In addition, recently, regulations for pollutant emission at sea have been strengthened, and accordingly, there is a growing interest in pollutant control technology [3,4]. Acid rain is defined as the accumulation of atmospheric acidic

substances in wet or dry conditions in the ecosystem. Acid rain refers to the ratio of chemicals in the air that combine with the rain to become acidified [1,3]. When the natural rain is in equilibrium with carbon dioxide in the atmosphere, the pH is lower than 5.6. Today, much more acidic rainfall is being observed all over the world. Acid rain is mainly caused by human release of sulfur and nitrogen mixtures that produce acidic reactivity in the atmosphere [5]. Sulfur dioxide and nitric oxide are air pollutants, which combine with the water vapor of the atmosphere to form acidic substances and acid rain. The acidic material is moved by the wind and becomes acid rain. The acid rain falls to a distance of about 4,023 km from where the pollutants are generated [6]. Acid rain made by humans damages lakes, forests, wildlife, and acidifies lakes to kill fish and other aquatic life. As the producer of the food chain is destroyed, the number of birds is reduced. It is because birds' food, insects, plants and aquatic life are killed by acid rain [7]. Not all areas where acid rain comes down have the same results. That is, the potential of the area capable of neutralizing acidic substances determines the amount of damage. Alkaline soil neutralizes acid. Therefore, areas with high alkaline soil are less damaging than those with neutral or acid soil. Several temporary measures have been taken to solve the acid rain problem, such as attempting to neutralize the acid by

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adding lime to the contaminated lake, but they have not had much effect. The solution to the acid rain problem is to remove pollutants that cause acid rain. We must reduce the use of fossil fuels such as coal, especially those containing a lot of sulfur. In order to protect forests, it is necessary to reduce the amount of automobile exhaust gas, use alternative energy, and use a lot of public transportation. This process can solve the acid rain problem [8].

The International Maritime Organization (IMO), under the United Nations (UN), announced that from 2016, the emission regulation at sea would be strengthened from the current Tier II to Tier III [9]. Accordingly, research and development on the removal of sulfur oxides (SO_x) and nitrogen oxides (NO_x) contained in gas discharged from vessels have been actively carried out, but there are still many problems to be solved. In addition, various researches to prevent the acidification of the soil due to acid rain and to create a more pleasant and affluent life (well-being culture) by decreasing the atmospheric concentration of sulfur oxides (SO_x) and nitrogen oxides (NO_x) [10]. Therefore, through this study, we tried to suggest a new method to solve the ultrafine dust problem and contribute to solving the acid rain problem. Especially, for smooth NO_x treatment, (1) first remove NO by oxidizing it to NO₂, and (2) finally remove NO₂ by absorption reaction using sodium hydroxide solution, which dissolves in alkaline solution, were suggested in this study

II. Experimental Background and Procedure

1. NO_x generation and reduction principle

It is known that various compounds exist in the nitrogen oxides depending on the bonding state of nitrogen and oxygen. Most of what is generated by combustion of fuel is NO and NO₂, and is generally referred to as NO_x (hereinafter referred to as NO_x). The ratio of NO/NO_x in the combustion gas discharged from the diesel engine combustion equipment is about 90 to 95%, and the NO_x in the exhaust gas is mostly NO [11]. NO is a colorless, odorless gas and hardly soluble in water. NO₂ is produced by oxidation of NO in the atmosphere, and it is converted to nitric acid (HNO₃) by binding with moisture, which is a main cause of acid rain. NO_x can be odorous even in the presence of 1 to 3 ppm, and it inhibits oxygen delivery by diminished immune responses by respiratory diseases and methemoglobin formation by reaction with blood hemoglobin. NO₂ is more soluble than NO, and when it is high, it is a reddish-brown irritant gas, which is five times more toxic than NO. Acute damage causes eye, nasal irritation and pulmonary hyperemia, pulmonary edema, obstructive bronchitis and pneumonia.

NO_x generated in the combustion process of the fuel is generated by the following two routes.

(1) Thermal NO_x: Nitrogen and oxygen in combustion

air react at high temperature to become NO_x. In this case, the higher the combustion temperature, the higher the O₂ in the combustibility, and the longer the residence time of the combustion gas in the higher temperature region, the more NO_x is generated [12].

(2) Fuel NO_x: When a portion of the nitrogen oxides contained in the fuel burns, it is oxidized to become NO_x, and there is almost no nitrogen (N) compound in the gaseous fuel [11,13].

Therefore, the following basic principle is applied to suppress the generation of NO_x.

- ① Lower the oxygen concentration in the combustion zone.
- ② Shorten the residence time of the combustion gas in the high temperature region.
- ③ Lower combustion temperature. Especially, local high temperature area should not be generated.
- ④ Using fuel containing less nitrogen

2. Traditional processes of NO_x reduction

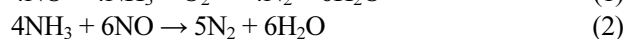
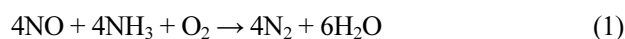
The most commonly used methods for treating nitrogen oxides are Selective Non-Catalytic Reduction (SNCR) and Selective Catalytic Reduction (SCR).

(1) Selective non-catalytic reduction (SNCR) [14-16]

The selective non-catalytic reduction method is a method in which a reducing agent containing nitrogen such as ammonia (NH₃) and urea (NH₂CONH₂) is injected at a temperature of about 870 to 1150°C, and the reduced reducing agent is ionized to react with nitrogen oxides. The ammonia and urea are separated according to the temperature range of the point where the reducing agent is injected by the method of decomposing into N₂, CO₂ and H₂O. When ammonia is injected, the reaction occurs at a lower temperature than when the urea is injected. Therefore, when the temperature of the injection point is low, ammonia is used. When this method is used, the removal efficiency of nitrogen oxide is about 50~70%

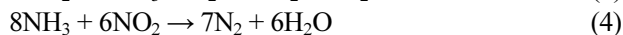
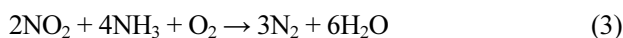
(2) Selective Catalytic Reduction (SCR) [17,18]

In the selective catalytic reduction method, exhaust gas and a reducing agent are simultaneously brought into contact with a catalyst layer at a temperature of 300 to 400°C, thereby, reducing NO_x in exhaust gas to nitrogen (N₂) and water vapor (H₂O) by selective reaction with a reducing agent (NH₃). The reducing agent used is ammonia water (mainly 25% ammonia solution), urea (50% urea solution), etc., injected into the front end of the SCR catalyst and injected into the exhaust gas. The reduction of NO_x in the SCR reactor is achieved by the following reaction.



Since most of the exhaust gas contains O₂ component, reaction (1) occurs, so NO and NH₃ react with each other

at a ratio of 1:1, and NH_3 is required as much as the NO reduction amount. In the exhaust gas, about 5% of the total NO_x is the NO_2 component, and the reaction formula is as follows.

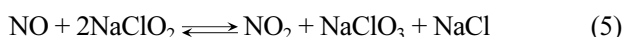


According to reaction (3), NH_3 is required twice as much as NO for NO_2 reduction, but the NO_2 content in the exhaust gas is as small as about 5%.

3. Our suggested processes of NO_x reduction

3.1 NO oxidation

As mentioned above, the NO_x in the exhaust gas emitted from the engine is largely divided into nitrogen oxide (NO) and nitrogen dioxide (NO_2). Of these, NO emissions account for the majority of NO_x emissions. Accordingly, for smooth NO_x treatment, NO is oxidized to NO_2 and removed. The oxidizing agent used here is sodium chlorite (NaClO_2). The chemical mechanism of the oxidation reaction using NaClO_2 is shown in the following reaction (5).

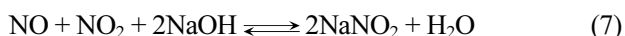


The formation of chlorine dioxide (ClO_2) gas is very important for the reaction of the above reaction formula (5) to be activated. It is known that NaClO_2 generates ClO_2 gas in the acidic range below pH 5 [19]. In the acidic region of NaClO_2 , the reaction of producing ClO_2 gas is as shown in the following reaction formula (6).



3.2 NO_2 absorption reaction

The NO_2 generated through the oxidation reaction is absorbed into the cleaning liquid to be removed. NO_2 is known to dissolve well in alkaline solution [20]. The mechanism of absorption reaction with sodium hydroxide (NaOH), which is a representative alkali solution, is shown in the following reaction formula (7).



When NO is oxidized to NO_2 , a reaction mechanism similar to that of reaction (7) is shown. At this time, nitric acid (HNO_3) is produced as a reaction product (see reaction 8). Therefore, in this experiment, the exact removal rate of NO gas was obtained by measuring pH and volume change of aqueous NaOH solution and titrating with standard acid solution (HCl) according to the formation of HNO_3 , resulting in determination of both HNO_3 and NO_2 concentrations and then obtaining NO_2/NO conversion ratio.

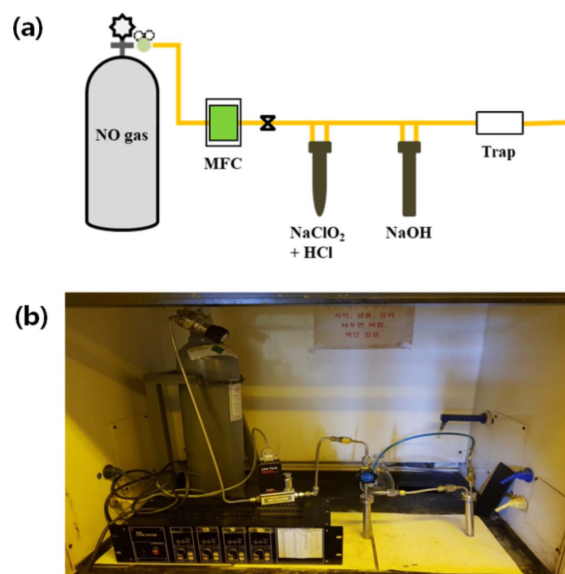
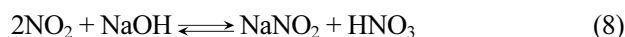


Figure 1. (a) Schematic diagram of NO oxidation and NO_2 absorption system used in this work, and (b) images of the actual home-made system.



4. Experimental set-up and materials

The NO_x used in this experiment was simulated using 3% $\text{NO}+97\%$ He gas mixture in consideration of the health of the experimenter and the laboratory environment. Sodium chlorite (NaClO_2), which is an oxidizing agent for NO oxidation, was used by diluting the powder with water to a concentration, and further added hydrochloric acid (HCl) was dissolved appropriately in accordance with pH. For adsorption reaction of NO_2 , sodium hydroxide (NaOH) was diluted with 40~60% aqueous solution. The supply of the simulated gas was maintained by MFC (Mass Flow Controller) and the range of NO gas flow rates were kept from 5 to 100 sccm. Figure 1(a) shows the schematic diagram of experimental setup used in this experiment. Figure 1(b) shows the actual home-made system. 3% $\text{NO}+97\%$ He gas mixture container, MFC & controller, NO oxidation chamber and NO_2 adsorption chamber can be seen from left side respectively.

5. Experimental method

Experiments were carried out by oxidizing NO to NO_2 and absorbing NO_2 as shown in Section 2.3., respectively. The aim of this study is to present the optimal NO_x treatment method by examining the change of NO oxidation reaction depending on oxidant concentration (1~10 M) change and oxidant pH (pH=1~5) change, which could control by adding HCl into NaClO_2 . In addition, we tried to suggest a method to improve NO_2 absorption by conducting NO_2 reduction reaction with reducing agent (NaOH) concentration (40~60%). For second step NO_2 reduction reaction, NO gas was also supplied (see reaction 3).

III. Results and Discussion

Figure 2(a) shows the changes of NO_2/NO conversion ratio according to the concentration of oxidant (NaClO_2). As the concentration of NaClO_2 increases under 100 sccm of the NO gas flow rate, NO is more oxidized to NO_2 . It is shown that NO oxidation can occur only when NaClO_2 concentration is more than 1 M. Figure 2(b) shows that under 10 M of the NaClO_2 concentration, the NO oxidation reaction occurs linearly with increasing NO gas flow rate, and the NO oxidation reaction can occur only when the NO gas flow rate is at least 5 sccm. Therefore, figures 2 (a) and (b) show that NO_2/NO conversion ratio of 20% can be obtained when the NaClO_2 concentration is 10 M and the NO gas flow rate is 100 sccm, respectively. However, this is much less efficient than selective non-catalytic reduction (50~60%). Since the wet reaction depends on various parameters (type of oxidizer and reducing agent, concentration, pH, reaction temperature, absorption method and titration method), therefore, we think that the removal efficiency can be greatly improved by adjusting the above variables well. This means that it is still necessary to develop a new concept adsorbent capable of adsorbing / removing the ultrafine dust which does not have the technology to completely remove the ultrafine dust.

As shown in Section 2.3, the formation of chlorine dioxide (ClO_2) gas, which can generate in the acidic range below pH 5 and control by adding HCl into NaClO_2 , is

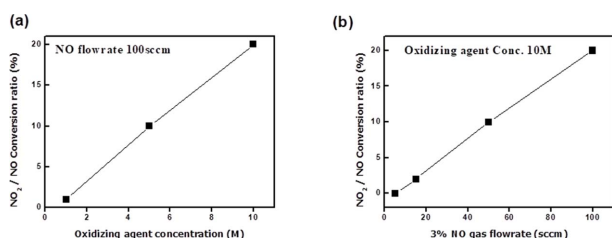


Figure 2. (a) The change of NO_2/NO conversion ratio according to the concentration of oxidizing agent, and (b) the change of NO_2/NO conversion ratio according to the NO gas flow rate at 10 M of oxidizing agent.

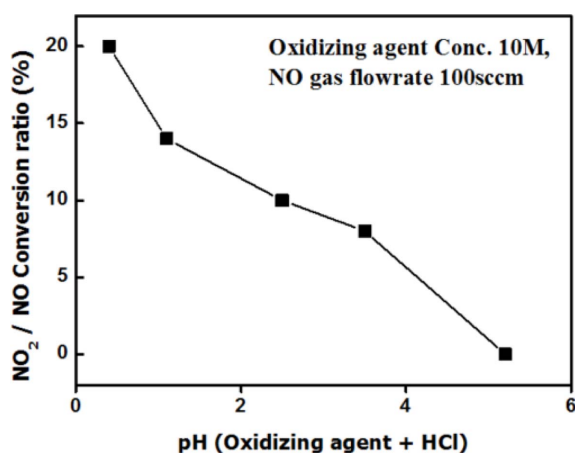


Figure 3. NO_2/NO conversion ratio vs. pH change.

very important for the reaction of NO oxidation. Figure 3 shows that NO is effectively oxidized to NO_2 as the pH of the oxidizing agent decreases with hydrochloric acid added to the oxidizing agent (NaClO_2). Also, when the pH is above 5, the NO oxidation reaction hardly occurs. This means that the lower the pH of the oxidant under the optimal conditions (i.e. NaClO_2 concentration: 10 M and NO gas flow rate: 100 sccm) as shown in figure 2, the more ClO_2 is generated and the NO oxidation reaction is further promoted.

Figure 4(a) shows that the higher the NaOH concentration, the more the NO_2 absorption (reduction) reaction occurs, and figure 4(b) shows that the pH of NaOH, the NO_2 absorbent, continues to decrease as the NaOH concentration increases. This means that the pH of the NaOH is reduced because the nitric acid (HNO_3) resulting from the NO_2 reduction reaction (see reaction (8) in Section 2.3) causes the neutralization reaction with NaOH to produce water continuously. Therefore, it is possible to determine the concentration of HNO_3 produced as a result of the NO_2 absorption reaction if the exact concentration is obtained by titrating with the standard acid solution (HCl) after accurately measuring the volume of the absorbent (NaOH) remaining after the reaction, and further, NO_2/NO conversion ratio was obtained. Based on these results, it was found that the removal efficiency of NO gas was up to 20% in this study.

Figure 5(a), similar to figure 4(b), shows that the pH of the absorbent NaOH decreases gradually as the concentration of oxidizing agent (NaClO_2) increases. Figure 5(b) also shows that the concentration of nitric acid (HNO_3) increases continuously as the concentration increases. This means that the NO removal efficiency is rather low, but it is a method that can easily remove NO gas with a relatively

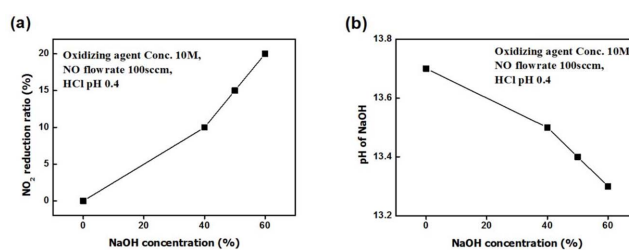


Figure 4. Changes of (a) NO_2 reduction ratio and (b) pH of NaOH with the NaOH concentrations.

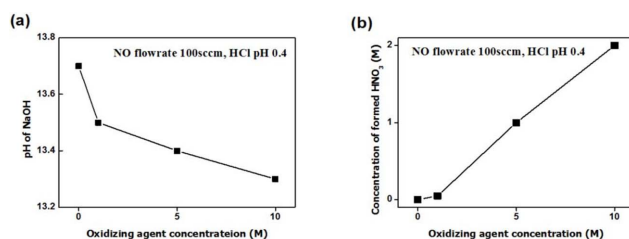


Figure 5. Changes of (a) pH of NaOH and (b) concentration of formed HNO_3 according to the concentrations of oxidizing agent.

simple device without existing large-scale expensive equipment. Therefore, our newly developed method can be applied to the capture and removal of ultrafine dust caused by air pollution in the future.

IV. Conclusions

It was found that NO removal efficiency increased as the concentration of oxidant increased (as the flow rate of NO gas increased by more than 100 scfm), and NO decreased more effectively as the pH of hydrochloric acid added to the oxidant was lower. The NO₂ uptake was better with increasing NaOH concentration, but the molar concentration (M) was more important than the NaOH concentration of 40% or more. It was found that the NO removal efficiency was ~20% lower than that of the selective NO reduction, suggesting that if we could precisely control the variable parameters of influencing the NO removal efficiency, more higher NO removal efficiency (possibly over 40%) than now would get. Indeed, this experimental method is expected to be a new method that can be applied to the capture and removal of ultrafine dust caused by air pollution because it is a method that can easily remove NO gas by a simple device without expensive giant equipment.

Acknowledgements

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