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

Hyeon Jin Seo\textsuperscript{a}, Rak Hyun Jeong\textsuperscript{b}, Jang-Heon Boo\textsuperscript{c}, Jimin Song\textsuperscript{c}, and Jin-Hyo Boo\textsuperscript{a,b}\*  
\textsuperscript{a}Department of Chemistry, Sungkyunkwan University, Suwon 16419, Korea  
\textsuperscript{b}Institute of Basic Science, Sungkyunkwan University, Suwon 16419, Korea  
\textsuperscript{c}Songnae High School, Bucheon 14741, Korea  

Received September 20, 2017; revised October 18, 2017; accepted November 21, 2017

Abstract This study was conducted to remove NO\textsubscript{x}, which is the main cause of fine dust and air pollution as well as acid rain. NO\textsubscript{x} was tested using 3% NO (diluted in He) as a simulated gas. Experiments were sequentially carried out by oxidizing NO to NO\textsubscript{2} and absorbing NO\textsubscript{2}. Especially, we focused on the changes of NO oxidation according to both oxidant (NaClO\textsubscript{2}) 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 NO\textsubscript{2} absorption by conducting NO\textsubscript{2} 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 NO\textsubscript{2} 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, NO\textsubscript{2} 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 \textmu m or less, it is referred to as “PM\textsubscript{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 acid 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

\*Corresponding author  
E-mail: jhboo@skku.edu
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 (SOx) and nitrogen oxides (NOx) 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 (SOx) and nitrogen oxides (NOx) [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 NOx 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. NOx 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 NOx (hereinafter referred to as NOx). The ratio of NO/NO2 in the combustion gas discharged from the diesel engine combustion equipment is about 90 to 95%, and the NOx 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. NOx 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 NOx 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.

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

(1) Thermal NOx: Nitrogen and oxygen in combustion air react at high temperature to become NOx. 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 NOx is generated [12].

(2) Fuel NOx: When a portion of the nitrogen oxides contained in the fuel burns, it is oxidized to become NOx, 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 NOx.

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 NOx 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 NOx 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 NOx in the SCR reactor is achieved by the following reaction.

\[
4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \quad (1)
\]

\[
4\text{NH}_3 + 6\text{NO} \rightarrow 5\text{N}_2 + 6\text{H}_2\text{O} \quad (2)
\]

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 NH₃ is required as much as the NO reduction amount. In the exhaust gas, about 5% of the total NOₓ is the NO₂ component, and the reaction formula is as follows.

\[ 2\text{NO}_2 + 4\text{H}_2\text{O} + 2\text{O}_2 \rightarrow 3\text{N}_2 + 6\text{H}_2\text{O} \quad (3) \]

\[ 8\text{NH}_3 + 6\text{NO}_2 \rightarrow 7\text{N}_2 + 6\text{H}_2\text{O} \quad (4) \]

According to reaction (3), NH₃ is required twice as much as NO for NO₂ reduction, but the NO₂ content in the exhaust gas is as small as about 5%.

### 3. Our suggested processes of NOₓ reduction

#### 3.1 NO oxidation

As mentioned above, the NOₓ in the exhaust gas emitted from the engine is largely divided into nitrogen oxide (NO) and nitrogen dioxide (NO₂). Of these, NO emissions account for the majority of NOₓ emissions. Accordingly, for smooth NOₓ treatment, NO is oxidized to NO₂ and removed. The oxidizing agent used here is sodium chlorite (NaClO₂). The chemical mechanism of the oxidation reaction using NaClO₂ is shown in the following reaction (5).

\[ \text{NO} + 2\text{NaClO}_2 \rightarrow \text{NO}_2 + \text{NaClO}_3 + \text{NaCl} \quad (5) \]

The formation of chlorine dioxide (ClO₂) gas is very important for the reaction of the above reaction formula (5) to be activated. It is known that NaClO₂ generates ClO₂ gas in the acidic range below pH 5 [19]. In the acidic region of NaClO₂, the reaction of producing ClO₂ gas is as shown in the following reaction formula (6).

\[ 5\text{NaClO}_2 + 4\text{HCl} \rightarrow 4\text{ClO}_2 + 5\text{NaCl} + 2\text{H}_2 \quad (6) \]

#### 3.2 NO₂ absorption reaction

The NO₂ generated through the oxidation reaction is absorbed into the cleaning liquid to be removed. NO₂ 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).

\[ \text{NO} + \text{NO}_2 + 2\text{NaOH} \rightarrow 2\text{NaNO}_2 + \text{H}_2\text{O} \quad (7) \]

When NO is oxidized to NO₂, a reaction mechanism similar to that of reaction (7) is shown. At this time, nitric acid (HNO₃) 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 HNO₃, resulting in determination of both HNO₃ and NO₂ concentrations and then obtaining NO₂/NO conversion ratio.

\[ 2\text{NO}_2 + \text{NaOH} \rightleftharpoons \text{NaNO}_2 + \text{HNO}_3 \quad (8) \]

### 4. Experimental set-up and materials

The NOₓ used in this experiment was simulated using 3% NO+97% He gas mixture in consideration of the health of the experimenter and the laboratory environment. Sodium chlorite (NaClO₂), 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 NO₂, 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% NO+97% He gas mixture container, MFC & controller, NO oxidation chamber and NO₂ adsorption chamber can be seen from left side respectively.

### 5. Experimental method

Experiments were carried out by oxidizing NO to NO₂ and absorbing NO₂ as shown in Section 2.3., respectively. The aim of this study is to present the optimal NOₓ 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 NaClO₂. In addition, we tried to suggest a method to improve NO₂ absorption by conducting NO₂ reduction reaction with reducing agent (NaOH) concentration (40–60%). For second step NO₂ reduction reaction, NO gas was also supplied (see reaction 3).
III. Results and Discussion

Figure 2(a) shows the changes of NO\textsubscript{2}/NO conversion ratio according to the concentration of oxidant (NaClO\textsubscript{2}). As the concentration of NaClO\textsubscript{2} increases under 100 sccm of the NO gas flow rate, NO is more oxidized to NO\textsubscript{2}. It is shown that NO oxidation can occur only when NaClO\textsubscript{2} concentration is more than 1 M. Figure 2(b) shows that under 10 M of the NaClO\textsubscript{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\textsubscript{2}/NO conversion ratio of 20% can be obtained when the NaClO\textsubscript{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\textsubscript{2}) gas, which can generate in the acidic range below pH 5 and control by adding HCl into NaClO\textsubscript{2}, is very important for the reaction of NO oxidation. Figure 3 shows that NO is effectively oxidized to NO\textsubscript{2} as the pH of the oxidizing agent decreases with hydrochloric acid added to the oxidizing agent (NaClO\textsubscript{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\textsubscript{2} concentration: 10 M and NO gas flow rate: 100 sccm) as shown in figure 2, the more ClO\textsubscript{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\textsubscript{2} absorption (reduction) reaction occurs, and figure 4(b) shows that the pH of NaOH, the NO\textsubscript{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\textsubscript{3}) resulting from the NO\textsubscript{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\textsubscript{3} produced as a result of the NO\textsubscript{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\textsubscript{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\textsubscript{2}) increases. Figure 5(b) also shows that the concentration of nitric acid (HNO\textsubscript{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
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 sccm), and NO decreased more effectively as the pH of hydrochloric acid added to the oxidant was lower. The NO\(_2\) 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

This work was partially supported by the CBDRC of the Sungkyunkwan University

References

[1] D. Kang and J.-E. Kim, J. Korean Med. Sci. 29, 621 (2014).
[2] H. Lee, J. Kim, C.-L. Myung, and S. Park, J. of Mechanical Science and Technology 23, 1591 (2009).
[3] A. G. Nord and K. Tronner, Water, Air and Soil Pollution 85, 2719 (1995).
[4] D. Harikishore, K. Reddy, and S.M. Lee, J. Environ. Anal. Toxicol. 2, 1 (2012).
[5] L. Bityukova, Water, Air, and Soil Pollution 172, 239 (2006).
[6] D.-S. Kim, J. Jeong, and J. Ahn, J. Korean Soc. Atmos. Environ. 32, 422 (2016).
[7] Sunita Bhargava and Sharad Bhargava, J. of Applied Chemistry 5, 19 (2013).
[8] I. A. Reşitoğlu, K. Altinisik, and A. Keskin, Clean Technol. Environ. Policy 17, 15 (2015).
[9] UNCTAD, Review of Maritime Transport 2016, United Nations Publications (2016) pp. 1-104.
[10] A. Singh and M. Agrawal, J. of Environmental Biology 29, 15 (2008).
[11] D. Shimokuri, S. Fukuba, and S. Ishizuka, Proceedings of the Combustion Institute 35, 3573 (2015).
[12] J. Odgers and D. Kretschmer, The American Society of Mechanical Engineers 2, 1 (1985).
[13] D.W. Pershing and J. O. L. Wendt, Symposium (International) on Combustion 16, 389 (1977).
[14] S. Mahmoudi, J. Baeyesn and J. P.K. Seville, Biomass and Bioenergy 34, 1393 (2010).
[15] S. W. Bae, S. A. Roh, and S. D. Kim, Chemosphere 65, 170 (2006).
[16] X. Han, X. Wei, U. Schnell, and K. R.G. Hein, Combustion and Flame 132, 374 (2003).
[17] M. F. Irfan, J. H. Goo, and S. D. Kim, Applied Catalysis B: Environmental 78, 267 (2008).
[18] N.W. Cant and A. D. Cowan, Catalysis Letters 46, 207 (1997).
[19] H. W. Hsu, C. J. Lee, and K. S. Chou, Chem. Eng. Comm. 170, 67 (1997).
[20] C. Baukal, Metal Finishing 103, 18 (2005).