Technical note

Oxidation characteristics of airborne carbon nanoparticles by NO₂

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ABSTRACT

The oxidation characteristics of airborne carbon nanoparticles were investigated at various temperatures and NO₂ concentrations. Airborne carbon nanoparticles were generated by spark-discharging method using nitrogen as a carrier gas. Monodisperse carbon particles classified using a differential mobility analyzer were introduced into a tube furnace with NO₂ for oxidation reaction. The size distributions of oxidized carbon aerosol particles were measured using a scanning mobility particle spectrometer system which consisted of a differential mobility analyzer and a condensation particle counter. The result was that as NO₂ concentrations and reaction temperatures increased, the surface oxidation rate of carbon aerosol particles increased. For NO₂ gas, the activation energy of the oxidation reaction was approximately 76.3 kJ/mol. The activation energy of the oxidation reaction for the mixture of NO₂ and O₂ gases was 65.9 kJ/mol, which is smaller than that for only NO₂ gas.

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1. Introduction

For over a century, diesel engines have proved reliable, economical and durable source of power for many applications. Currently, diesel vehicles are undergoing further development due to their higher fuel efficiency and lower CO₂ emissions as compared to gasoline vehicles because regulations concerning diesel vehicles are becoming more severe due to the harmful effects of diesel exhaust on human health and on the environment (Utell and Frampton, 2000; EPA600/8-90/057F, 2002). The particulate matter (PM) from diesel vehicles consists mostly of carbonaceous particle and a volatile organic fraction (VOF). The PM is often formed during combustion process in locally fuel-rich regions and exhausted in the form of solid agglomerates condensed with VOC (Walker, 2004).

For diesel engine, the lowering of PM emission is generally based on a filtration system in which trapped PM is periodically removed by means of controlled oxidation reaction with pure O₂ or air. Accordingly, many researchers have investigated the oxidation characteristics of PM exhausted from the diesel engine. Higgins et al. (2002, 2003) investigated the oxidation characteristics of size-selected soot nanoparticles in air with the temperature range of 800–1140 °C. However, according to recent research, NO₂ has been found to be a more efficient oxidant than O₂ at lower temperatures in the range of 200–500 °C (Dorai et al., 2000; Ehrburger et al., 2002; Jeguirim et al., 2005; Kamm et al., 2004).
Small amounts of NO₂ in the range of a few hundred ppm by volume can promote the continuous oxidation of carbon particulates. In most regenerative diesel particulate filters (DPF) using NO₂, NO₂ is produced by catalytic oxidation reactions or non-thermal plasma reactions of NO, which is previously present in the engine exhaust stream (Dorai et al., 2000; Ehrburger et al., 2002). Jeguirim et al. (2005) studied the oxidation of carbon black deposited on a quartz plate by NO₂ regarding the mass change of carbon black and the concentration of generated CO₂ and CO. Kamm et al. (2004) investigated the gasification of soot deposited on a quartz wool filter by O₃ and NO₂.

Most investigations of carbon oxidation by NO₂ have been on the carbon deposited on filters or plates. However, little is known about the oxidation characteristics of the carbon nanoparticles in aerosol state. In this study, we have focused on the oxidation of airborne carbon nanoparticles which are generated by a spark discharge generator. During the regeneration process of a DPF, the NO₂ can oxidize not only the soot collected on a DPF but also airborne PM emitted from the engine and redispersed from a DPF. This oxidation effect of PM by NO₂ in the airborne state could reduce the total PM emission as a concurring way for mitigation of PM emission.

In our experiment, the oxidation characteristics of nanosized carbon aerosol particles in NO₂ gas and in the mixture of NO₂ and O₂ gases were investigated at various temperatures. Additionally, the enhancement of carbon oxidation by NO₂ in the presence of O₂ was investigated because in the exhaust stream of diesel engines, a large excess of O₂ is always present compared to NO₂.
2. Materials and methods

Fig. 1 shows the experimental setup, consisting of three parts: generation of carbon aerosol nanoparticles; oxidation reaction using tube furnace with well-controlled temperature and measurement of particle size distribution.

Carbon nanoparticles are generated using a spark discharge aerosol generator, shown in Fig. 2 (Kim et al., 2006). Graphite rods (Alfa Aesar # 10135; Φ 6.3 mm, ≥99%, 2.25 g/cm³) were used as electrodes and micrometers were connected to the rods to adjust the gap distance precisely. As a carrier gas, N₂ gas was used to ensure a non-chemical reaction with the carbon vapor; its flow rate was maintained at 300 cm³/min. A high-voltage power supply (Korea Switching, Korea) was used to generate sparks. Electrical energy was stored in a capacitor of an electric circuit and the energy was then discharged between the electrodes at periodic frequencies. In an electric circuit, the resistance and capacitor were 500 kΩ and 0.0064 μF, respectively. The electrodes were locally heated by electrical sparks between two graphite electrodes when electrical energy was discharged sporadically (Schwyn et al., 1988). The heat from the sparks evaporated part of the carbon electrodes. The vaporized carbon was condensed due to the rapid cooling and carbon particles formed by nucleation, condensation and coagulation processes. Fig. 3 shows the particle size distribution for the condition of a gap distance of 0.5 mm and current of 1 mA. In this condition, the geometric mean diameter (GMD), geometric standard deviation (GSD) and number concentration were 62.2 nm, 1.67, and 4.8 × 10⁶ particles/cm³, respectively.

The differential mobility analyzer (DMA) is the traditional instrument for sizing aerosol particles. A simplistic description of the DMA is that the instrument is just two charged concentric cylinders with an inlet slit and a sampling slit. The DMA separates particles based on their electrical mobility. This electrical mobility diameter is defined as the diameter of a singly-charged particle with the selected electrical mobility. Aerosol particles for sizing are inserted into the annular region between the two cylinders at the inlet slit. They are carried by clean air flowing through the annular region. Particles with mobilities in a certain narrow range are sampled at the sampling slit. Using this DMA, monodisperse carbon nanoparticles with specific size (or electrical mobility) can be extracted. A condensation particle counter (CPC) measures the number of ultra-fine particles. The CPC operates on the principle of enlarging small particles using a condensation technique to form droplets that are large enough to be detected optically. The scanning mobility particle spectrometer (SMPS) system consists of DMA and CPC. The aerosol particle flow is sampled directly into the DMA for particle size classification and particle counting by the CPC. The data are then sent to the internal, single-board computer for processing and storage. From this repeated process, the SMPS system provides the particle size distribution with a maximum 128 channels of size resolution.

In Fig. 1, the polydisperse carbon nanoparticles generated by the spark discharge aerosol generator were sent to a first DMA (3071, TSI Inc., USA) to extract monodisperse aerosol particles. The extracted flow (300 cm³/min) containing classified particles merged in the aerosol mixer with a mixture gas (1200 cm³/min) of NO₂ and O₂. The relative flow rates of mixed gases including NO₂, N₂ and O₂ were controlled using mass flow controllers (MFC; Mykrolis, FC-280S, USA). Then, the total flow rate (1500 cm³/min) was passed into the hot-walled tube furnace. Oxidation reaction of carbon nanoparticles by NO₂ occurred in the hot-walled tube furnace at various temperatures. The inner diameter and length of the quartz tube were 36 mm and 600 mm, respectively. The spatial temperature distributions of
the furnace for various set temperatures are shown in Fig. 4. A second DMA (3085, TSI Inc., USA) and a condensation particle counter (CPC; 3776, TSI Inc., USA) were used for measuring the size distribution after the oxidation reaction.

The oxidation rates of the nanoparticles by NO\textsubscript{2} were calculated based on the particle size distribution data. The experimental conditions for oxidation by only NO\textsubscript{2} were within a temperature range of 17–700 °C and NO\textsubscript{2} concentration range of 0–552 ppm. For oxidation by NO\textsubscript{2} in the presence of O\textsubscript{2}, a fixed mixture gas concentration of 317 ppm of NO\textsubscript{2} and 9.6% of O\textsubscript{2} was used.

### 3. Results and discussion

Fig. 5 shows the particle size distributions with various temperatures at NO\textsubscript{2} concentration of 166 ppm and classified particle diameter of 81 nm. As reaction temperature increased, particle size decreased. Oxidation of aerosol-phase carbon nanoparticles in pure air was negligible in the temperature range of 200–700 °C. Fig. 6 shows variations of the geometric mean diameter (GMD) of carbon nanoparticles with initial particle diameter of 41 nm and 81 nm at various NO\textsubscript{2} concentrations and temperatures. As the temperature and NO\textsubscript{2} concentration increased, the GMD of nanoparticles decreased exponentially.

From this variation of GMD of carbon nanoparticles, we calculated the GMD decrease ratio as follows:

\[
\text{GMD decrease ratio} = \left(1 - \frac{\text{GMD after oxidation}}{\text{GMD before oxidation}}\right) \times 100. \tag{1}
\]

The variations of GMD decrease ratio according to various NO\textsubscript{2} concentrations and temperatures are shown in Table 1. As temperature and NO\textsubscript{2} concentration increased, the GMD decrease ratio also increased. GMD decrease ratio increased to approximately 30% when increasing the NO\textsubscript{2} concentration at a temperature of 700 °C although the GMD decrease ratio was below 3% at temperatures below 300 °C. This implies that the oxidation effect of the carbon nanoparticles at low temperatures was smaller than that at high temperatures. At 0 ppm of NO\textsubscript{2} concentration, the GMD of carbon nanoparticles decreased slightly. This could be due to the evaporation of impurities of carbon nanoparticles or restructuring effect of carbon nanoparticles in the furnace.

The surface oxidation rate, which is the mass decrease ratio per unit surface area of particles by oxidation reactions, is calculated from the particle size distribution data of soot nanoparticles.

The overall mechanisms of carbon oxidation by NO\textsubscript{2} are as follows:

\[
\text{C} + 2\text{NO}_2 \rightarrow \text{CO}_2 + 2\text{NO} \tag{2}
\]

\[
\text{C} + \text{NO}_2 \rightarrow \text{CO} + \text{NO} \tag{3}
\]

The surface reaction of C (carbon active site) with NO\textsubscript{2} release CO, CO\textsubscript{2} and NO (Jeguirim, M. et al., 2005). Therefore, the equation below indicates the oxidation rate.

\[
\text{rate} = k[C]^a[\text{NO}_2]^b \tag{4}
\]

where, \(k\) is the rate constant, \(a\) and \(b\) are the reaction orders of each material concentrations, [C] and [NO\textsubscript{2}] are the
concentrations of C and NO\textsubscript{2}, respectively. The rate constant is follows the Arrhenius equation (Stanmore et al., 2001; Ehrburger et al., 2002):

$$k = A e^{-E_a/RT}$$

(5)

where, \(A\) is the pre-exponential factor, \(R\) is the gas constant, and \(E_a\) is the activation energy. The activation energy is the minimum amount of energy required to activate atoms or molecules to a condition in which they can undergo chemical transformation or physical transport. Using the data for diameter decrease ratio of carbon nanoparticles, the surface oxidation rate, \(\text{rate}\), can be expressed as:

$$\text{rate} = \frac{m_{\text{in}} - m_{\text{out}}}{A_s dt}$$

(6)

where, \(m_{\text{in}}\) is the mass of a particle entering the furnace, \(m_{\text{out}}\) is the mass of a particle at the furnace outlet, \(A_s\) is particle surface area, and \(dt\) is residence time in the furnace (Higgins et al., 2002). The particle mass and surface area are calculated with the assumption that the morphology of carbon nanoparticles is spherical although actual carbon nanoparticles are fractal-like.

Fig. 7 shows that as the NO\textsubscript{2} concentration increased the surface oxidation rate of the carbon nanoparticles increased.

Table 2 shows the variation of the GMD decrease ratio in several cases of mixed NO\textsubscript{2} and O\textsubscript{2} concentrations at various temperatures. Especially, the oxidation rate by NO\textsubscript{2} in the presence of O\textsubscript{2} is higher than that without O\textsubscript{2}. Fig. 8 shows the logarithmic surface oxidation rates for the mixture of NO\textsubscript{2} and O\textsubscript{2}. For a mixed condition of NO\textsubscript{2} and O\textsubscript{2}, the activation energy was 65.9 kJ/mol. This activation energy is lower than that in NO\textsubscript{2} only. This decreased activation energy is very favorable for the oxidation effect of carbon nanoparticles by NO\textsubscript{2} because remaining O\textsubscript{2} always ranges from about 0.3% to 17% in real diesel engine exhaust gas (Schrenk and Berger, 1941).

In this study, we investigated the oxidation of carbon nanoparticles by NO\textsubscript{2}. Under the assumption of spherical particles, we calculated the surface reaction rate and activation energy of carbon nanoparticles. As real diesel particles are fractal-like and consist of various organic components, they could affect the effective density and the oxidation rate of particles. Because of the agglomerate structure of the diesel particles, their effective density is lower than that of spherical particles. This could lead to a higher rate of observed size reduction for the fractal-like particles. Moreover, the amount of hydrogen in organic components on the surface of diesel particles could lead to a higher oxidation rate (Higgins et al., 2002). Finally, this increasing surface reaction rate of diesel particles might be expected to have a significantly lower activation energy.

4. Conclusions

In this research, the oxidation characteristics of airborne carbon nanoparticles were investigated in various temperatures and NO\textsubscript{2} concentrations. The carbon oxidation rates were dependent on particle size, temperature and NO\textsubscript{2} concentrations. The
surface oxidation rate of carbon nanoparticles by NO$_2$ and a mixture of NO$_2$ and O$_2$ increases exponentially. As the NO$_2$ concentration becomes higher and the particle size becomes larger, the surface oxidation rate increases with increasing surrounding temperatures. However, the oxidation rate by NO$_2$ in the presence of O$_2$ is higher than that without O$_2$.

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