Kinetics of Soot Oxidation by NO₂

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Modern technologies use NO₂ to promote low-temperature soot oxidation for diesel particulate filter regeneration. In this study, the online aerosol technique of high-temperature oxidation tandem differential mobility analysis is used to study kinetics of soot oxidation by NO₂. Soot particles are exposed to varying temperature and NO₂ mixing ratio inside the furnace resulting from thermal decomposition of NO₂ to NO. This causes soot oxidation rates to vary throughout the furnace. Variations in temperatures and NO₂ mixing ratio are thoroughly accounted for the first time. Soot oxidation rates are calculated as a function of frequency factor 

\[ A_{soot} \text{ activation energy } E_{soot} \text{ and concentration of NO}_2 \text{ within the furnace at temperatures ranging from 500 to 950 °C. Results suggest } A_{soot} \text{ and } E_{soot} \text{ values for soot oxidation of } 2.4 \times 10^{-14} \text{ (mm K}^{-1} \text{ cm}^{-3} \text{ molecule}^{-1}) \text{ and 47.1 kJ mol}^{-1} \text{, respectively, when reaction order to NO}_2 \text{ is assumed as unity. The activation energy for soot oxidation with NO}_2 \text{ is significantly lower than oxidation with air. However, parts per million levels of NO}_2 \text{ cause soot oxidation at low temperatures suggesting NO}_2 \text{ is a stronger oxidant than O}_2.\]

1. Introduction

Soot has a controlling influence on earth’s temperature and climate. In addition, soot particles pose significant human health risk. Elimination of soot particle emissions from diesel engines has attracted lots of attention because of potential health risk around urban areas. Soot particles could be reduced either by modifying the combustion process inside the engine or by removing particles from the exhaust stream. Particles are removed from the exhaust stream using a diesel particulate filter (DPF), followed by catalytic soot oxidation to regenerate the filter (1). For these reasons, it is of immense interest to understand the kinetics of soot oxidation in the presence of oxidants like NO₂ and O₂ at temperatures relevant to both in-cylinder and exhaust after-treatment conditions. The high temperature (>800 °C) soot oxidation studies are relevant to modeling soot oxidation inside an engine cylinder or at flame conditions, while the low temperature (300–700 °C) soot oxidation studies are useful in understanding soot oxidation in the diesel exhaust and after-treatment systems such as diesel particulate filters (DPF) (2). Regeneration of DPF is performed at low temperatures (300–450 °C) to avoid thermal fatigue of the devices and to minimize energy used for regeneration.

Although there are other oxidants present during diesel soot combustion, a majority of soot oxidation studies were done under oxygen environment or air (2–5). Stanmore et al. (6) reviewed soot oxidation by NO₁ (NO₂, NO, and N₂O). They reported the magnitude of soot oxidation reaction rates are in the order of NO₂ > N₂O ≈ NO ≈ O₂, showing NO₂ oxidation most prominent. NO₂ is a stronger oxidant than O₂ promoting low temperature oxidation of soot in the range of 200–500 °C (7). NO₂ has also been postulated to have a synergistic role with NO in the combustion of diesel soot (7, 8). Typically, NO₂ is 5–15% of the total NO (less than 50 ppm) in the diesel exhaust. However, oxidation catalysts like Pt could oxidize NO to NO₂ increasing NO₂ mixing ratio to 50% of the total NO, in the temperature range of 300–350 °C (7, 9). The continuously regenerating trap (CRT) (10) in diesel exhaust after-treatment system combines two chemical processes: platinum catalyzed oxidation of NO to NO₂ and oxidation of trapped soot in the presence of NO₂. Thus, it is of interest to better understand kinetics of soot oxidation in the presence of NO₂.

Most of the previous research studied soot oxidation using offline methods such as thermo-gravimetric analysis (TGA) (8, 11, 12). However, this method is subject to mass and heat transfer effects that make the quantification of kinetics of soot oxidation difficult. Bulk sample of soot particles is packed by unknown packing ratio. A reasonable decoupling for mass transfer effect is achieved by measuring diffusion coefficient through the bulk sample (13). However authors are not aware of good methods to decouple heat transfer effect from bulk sample. The best experimental approach was to put quartz chips in the bulk sample and assume the temperature is uniform (14). The advantage of current TDMA (Tandem Differential Mobility Analyzer) method is to determine reaction rate by looking at size change of primary particles decoupling mass and heat transfer effects to begin with. Higgins et al. (3, 4) studied kinetics of soot oxidation from ethylene diffusion flame and from exhaust stream of medium-duty diesel engine over the temperature range of 800–1000 °C in the presence of air as an oxidant. They used the online aerosol technique of high-temperature oxidation tandem differential mobility analysis (HTO-TDMA). This technique offers several advantages over previous offline methods, such as thermogravimetric analysis (TGA) (8, 11, 12). The HTO-TDMA method minimizes effects of transport and soot aging (5). Choo et al. (15) derived oxidation characteristics of spark-discharge generated soot in the presence of NO₂ using the HTO-TDMA method. However, they made significant errors in their analysis, which will be discussed in detail at the discussion section.

In this work, kinetics of soot oxidation using NO₂ as the primary oxidant are investigated using the HTO-TDMA method (3–5), at furnace temperatures ranging 500–950 °C. NO₂ inlet mixing ratios are varied from 0–600 ppm using N₂ as a carrier gas. A complication in using HTO-TDMA method to study soot oxidation with NO₂ using N₂ as a carrier gas is that NO₂ mixing ratios are not uniform throughout the heated length of the furnace. NO₂ decomposes to NO under N₂ environment inside the tube furnace at temperatures exceeding 500 °C under experimental conditions of this study. NO₂ decomposition in the tube at higher temperatures is modeled using a second order kinetic rate equation. This allows calculation of NO₂ concentration at each axial location throughout the heated length of the furnace. It is noteworthy...
that NO₂ concentration depends on thermal expansion of the heated gas within the tube in addition to thermal decomposition of NO₂ while NO₂ mixing ratio (mole fraction in ppm) is independent of thermal expansion and changes only caused by thermal decomposition of NO₂. The kinetic parameters for soot oxidation are derived as a function of nonuniform NO₂ concentrations and temperature in the furnace. The derived kinetic parameters are compared to other studies and implications for future research are discussed.

2. Experimental Method

Polydisperse soot particles are generated by a diffusion flame burner using ethylene as fuel. Particles are sampled through a 1 mm orifice drilled at the bottom of a horizontal 11 mm inner diameter stainless steel sampling tube. Soot particles are diluted and quenched by a constant flow of 5 liters per minute (Lpm) of N₂ through the sampling probe. Secondary dilution of the aerosol flow is done using an ejector dilutor (Air-Vac TD-110H vacuum transducer pump) with N₂ flow of about 20 Lpm at 30 psi as shown in Figure 1. Soot particles sent to differential mobility analyzer DMA-1 (TSI 3081 series long column DMA) for size selection based on electrical mobility. Size-selected monodisperse soot particles from the first DMA are then oxidized in a high temperature flow reactor and the resulting particle size distribution is measured using the second DMA with a condensation particle counter (CPC) as the detector. The second DMA is a nano-DMA (TSI 3085 series nano-DMA) designed to reduce particle losses of nanoparticle and improve size resolution in the range 3–50 nm (16). As shown in Figure 1, a parallel line bypassing the furnace is used to periodically monitor the size and concentration of monodisperse particle stream from DMA-1 at the beginning of each measurement. The bypass line ensures that flame conditions, and particle sizing from DMA-1 are constant throughout the experiment. Our setup is modified from the first DMA-2–3, respectively, at any given axial location with 

3. Modeling

Higgins et al. (3) fitted kinetic parameters in terms of observed decrease of peak particle size in the furnace from size distributions measured by the TDMA, using a nonlinear least-squares fit to experimental data. Using CFD simulations, Shrivastava et al. (18) showed that decrease in peak particle diameter was independent of diffusion and thermophoretic effects and served as a reliable parameter to derive soot oxidation rate within the furnace. Decrease in particle diameter is empirically described using a modified form of Arrhenius expression to account for variable NO₂ concentrations within the furnace following Stanmore et al. (2) given as:

\[ \dot{D}_p = -A_{\text{soot}}T^{7/2} \exp \left( \frac{E_{\text{soot}}}{RT} \right) [\text{NO}_2]^{n} \]

where \( \dot{D}_p \) is the rate of decrease of particle diameter with time, \( A_{\text{soot}} \) is frequency factor, \( E_{\text{soot}} \) is activation energy, \( R \) is the universal gas constant, \( T \) and [NO₂] are the absolute furnace temperature in K and the concentration of NO₂ in molecules cm⁻³, respectively, at any given axial location with the furnace, and \( n \) is the reaction order of soot with respect to NO₂. The exponent of temperature is held fixed at 0.5 to roughly account for dependence of collision frequency on temperature (3). The reaction order \( n \) should be experimentally determined. Various authors reported the reaction order for oxidation of soot with NO₂ as unity (\( n = 1 \))(12, 19). In the present study, the reaction order could not be determined experimentally as soot is subjected to changing...
NO\textsubscript{2} concentrations in the furnace. Hence, the reaction order is assumed to be 1 consistent with other studies.

The total decrease in particle size by oxidation in the furnace is found by integrating eq 2 along the furnace length

$$\Delta D_p = \int_0^x \frac{D_p(x)}{u(x)} dx$$  \hspace{1cm} (2)

where x is horizontal position in the tube, X is length of the tube, and u(x) is the flow velocity which varies linearly with temperature along the tube length.

Temperatures are measured using a K-type thermocouple at different furnace set-point temperatures as described by Higgins et al. (3) at gas flow rate of 0.5 Lpm. Figure 2 shows the measured temperature profile at furnace set-point temperatures of 850 °C. A fourth-order polynomial fit to measurements is used to describe the axial temperature profile throughout the furnace. As shown in Figure 2, temperature is maximum near the middle of the furnace and decreases to room temperature near the inlet and exit of the furnace.

NO\textsubscript{2} balanced in N\textsubscript{2} as a carrier gas is used. At temperatures higher than 500 °C, NO\textsubscript{2} decomposes to NO as a function of temperature and residence time within the furnace. The thermal decomposition of NO\textsubscript{2} is described by the following equation:

$$\text{NO}_2 + \text{NO}_2 \rightarrow \text{O}_2 + \text{NO} + \text{NO}$$  \hspace{1cm} (3)

The rate expression k(T) for eq 3 is defined as:

$$k(T) = A_{\text{NO}_2}\exp\left(-\frac{E_{\text{NO}_2}}{RT}\right)$$  \hspace{1cm} (4)

k(T) is the second-order rate constant in cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1}, A\textsubscript{NO\textsubscript{2}} is the frequency factor, and E\textsubscript{NO\textsubscript{2}} is the activation energy.

At any axial location within the furnace, the values of NO\textsubscript{2} concentration could be calculated as function of time and temperature using eqs 4 and 5 given as:

$$\frac{1}{N_t} = 2k(T)t + \frac{1}{N_0}$$  \hspace{1cm} (5)

where N\textsubscript{t} is the NO\textsubscript{2} concentration (molecules cm\textsuperscript{-3}) at given axial location, t is the time in seconds spent by particles up to that location, and N\textsubscript{0} is the inlet concentration of NO\textsubscript{2} to the furnace at time zero.

Values of A\textsubscript{NO\textsubscript{2}} and E\textsubscript{NO\textsubscript{2}} for eq 4 have been experimentally determined by Park et al. (20). In this study, NO\textsubscript{2} decomposition within the furnace is measured at different temperatures ranging from 500 to 950 °C at inlet NO\textsubscript{2} mixing ratios of 200 and 600 ppm. Measurements are compared to predicted NO\textsubscript{2} decomposition within the furnace using eq 4 and 5 and value of E\textsubscript{NO\textsubscript{2}} (116 kJ mol\textsuperscript{-1}) suggested by Park et al. (20). The value of A\textsubscript{NO\textsubscript{2}} used in eq 4 is found by fitting to 10 measurements of NO\textsubscript{2} decomposition in the furnace. The fitted A\textsubscript{NO\textsubscript{2}} (1.59 × 10\textsuperscript{-11} cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1}) is a factor of 2 higher than corresponding value from Park et al. (20) (7.49 × 10\textsuperscript{-12} cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1}), but within expected range of uncertainty of A\textsubscript{NO\textsubscript{2}} (20). Figure 2 shows the calculated NO\textsubscript{2} mixing ratios throughout the heated length of the furnace using eqs 4 and 5. As shown in Figure 2, NO\textsubscript{2} mixing ratio decreases at high temperature in the furnace. It is noteworthy that influence of radial temperature distribution and resulting NO\textsubscript{2} decomposition on soot oxidation is not considered in the present analysis. Our previous study using comprehensive Computational Fluid Dynamics modeling (18) showed that limitations in measurement of accurate radial gas temperature profile in the laminar flow reactor may cause a factor of 2 uncertainty in derived soot oxidation rates. This uncertainty is mainly reflected in value of frequency factor, but does not affect the activation energy for soot oxidation. More accurate analysis would require CFD analysis similar to our previous study, but is beyond the scope of this work.

Soot particles are exposed to nonuniform temperature and oxidant (NO\textsubscript{2}) mixing ratios in the furnace. Assuming a reaction order of 1, values of A\textsubscript{soot} and E\textsubscript{soot} in eq 1 were first determined by fitting to 15 different values of measured \Delta D_p at varying furnace set-point temperatures (500–950 °C) and inlet NO\textsubscript{2} mixing ratios (200–600 ppm). Figure 3 shows the quality of fits to measured decrease in particle diameter (\Delta D_p). Figure 2 also shows the varying soot oxidation rates (dD_p/dt) on the right-hand y-axis, calculated from the fits. As shown in Figure 2, the instantaneous soot oxidation rate varies throughout the heated length of furnace as function of temperature and NO\textsubscript{2} mixing ratio. The modeling approach described above systematically accounts for varying soot oxidation rates within the furnace.

4. Results

Figure 4 shows representative TDMA scans from the nano-DMA for particles of initial size 40 nm. Figure 4a shows that particle size distribution shifts to smaller sizes with increasing inlet NO\textsubscript{2} mixing ratio at constant furnace set-point temperature of 800 °C. Figure 4b shows decrease of particle sizes at constant inlet NO\textsubscript{2} mixing ratio of 400 ppm and increasing furnace temperatures. Thus particles shrink because of oxidation with both increasing temperatures and increasing oxidant levels. The broadening of particle size distribution with oxidation is because of particles experiencing a range of residence times within the reactor. The varying residence time distribution of particles is because of near-laminar gas flow, buoyancy-induced secondary flows at higher furnace temperatures, and effects of thermophoresis (18). Following previous works (3–5), the results in this study were analyzed with respect to \Delta D_p/\Delta t, where \Delta D_p is the change in peak...
mobility diameter and $\Delta t$ is the characteristic residence time within the reactor.

Table 1 shows the measured $\Delta D_p$ values at different temperatures and inlet NO$_2$ mixing ratios within the furnace. Interestingly, particles show modest size reduction even at zero NO$_2$ mixing ratios when nitrogen is the carrier gas at higher furnace temperatures. For example, at 950 °C, the decrease in peak mobility diameter under nitrogen environment is 8 nm. Nienow et al. (5) observed a size reduction of 4.3 nm at 975 °C for soot particles of initial size 30 nm from ethylene diffusion flame. However, Nienow et al. (5) used an aerosol flow rate of 1 Lpm through the same tube geometry as the present study; hence, particle residence times were shorter as compared to the present study. The 40 nm particles are near-spherical, so effects of thermally induced restructuring of aggregates at high temperatures is less likely (5). In this work, the soot particles are found to have significant organic carbon content (OC) in addition to elemental carbon (EC). A thermal-optical analysis on the polydisperse soot particles collected on a quartz filter from the flame indicated that OC could be up to 40% of the total carbon (TC). This measurement includes artifacts (including gas phase organics in addition to particle phase). Most of the semivolatile OC would evaporate because of further dilution in the DMA-1 and at furnace temperatures below 500 °C and would not contribute to soot oxidation under experimental conditions in this study. However, some organics, such as PAHs, may be strongly adsorbed on the soot particles. It is plausible that evaporation of strongly adsorbed relatively nonvolatile OC and decomposition of oxygen containing functional groups (21, 22) could be responsible for size reduction observed under N$_2$ environment without NO$_2$ consistent with conclusion of Nienow et al. (5).

To derive oxidative kinetics of soot oxidation, it is necessary to separate the nonoxidative size reduction from calculations of $\Delta D_p$. Following Nienow et al. (5), it is assumed that the oxidative and nonoxidative components of $\Delta D_p$ are additive. Hence, the oxidative component of $\Delta D_p$ is derived by subtracting the $\Delta D_p$ measured under N$_2$ environment from total $\Delta D_p$ measured at any given NO$_2$ mixing ratio as shown in Table 1. Choo et al. (15) derived oxidation rate parameters without accounting for the nonoxidative component of $\Delta D_p$, hence their results may be biased.

Measurements yielded fifteen values of oxidative $\Delta D_p$ at five different furnace temperatures and three inlet NO$_2$ mixing ratios as shown in the last three columns of Table 1. As described earlier, predictions of $\Delta D_p$ are derived corresponding to each inlet NO$_2$ mixing ratio and furnace temperature using eqs 1 and 2. The values of $A_{\text{soot}}$ and $E_{\text{soot}}$ are derived from fitting the calculated values of $\Delta D_p$ to the five measurements assuming reaction order $n$ to be 1. Table 2 reports the fitted kinetic parameters for soot oxidation using NO$_2$ as the oxidant under N$_2$ environment.

5. Discussion

As shown in Table 2, value of activation energy for soot oxidation $E_{\text{soot}}$ is 47.1 kJ mol$^{-1}$ assuming a reaction order of unity for soot oxidation with NO$_2$. This value is lower than $E_{\text{soot}}$ values reported by prior studies. For example, Kamm et al. (12) derived a value of 73.1 ± 6 kJ mol$^{-1}$ as the activation energy for soot from spark generator collected on quartz wool plugs and exposed to 1000 ppm NO$_2$ at 200–350 °C. They reported nonlinearity in their Arrhenius plot indicating different reaction mechanism with higher activation energy at higher temperatures. Kamm et al. (12) used a 3-parameter fit for just four data points at four temperatures; hence, their fitting may be biased. Choo et al. (15) derived an activation energy of 76.3 kJ mol$^{-1}$ for spark discharge soot oxidation with NO$_2$ using the HTO-TDMA method in the temperature range 200–700 °C. However, they did not account for nonoxidative/evaporative components of $\Delta D_p$ as described earlier. In addition, Choo et al. (15) used an incorrect approach of deriving the value of $E_{\text{soot}}$ from the Arrhenius plot without considering effects of varying soot oxidation rates within the furnace as function of changing temperature and NO$_2$ concentrations. For example, for the experimental conditions of Choo et al. (15), NO$_2$ mixing ratios are calculated to decrease by up to 27% at 700 °C inside the furnace using $A_{\text{soot}}$, and $E_{\text{soot}}$ values in the present study.

To compare our results with that of Choo et al. (15), it is necessary to reanalyze their NO$_2$ oxidation data in the same way as done here. Thus, the NO$_2$ oxidation data from Choo et al. (15) in their Table 1, and temperature distribution inside the furnace in their Figure 4 are chosen. For consistency, only data for three temperatures 500, 600, and 700 °C are chosen. The change in diameter $\Delta D_p$ is calculated as function of inlet NO$_2$ mixing ratios of 166, 386, and 552 ppm from

<p>| TABLE 1. Measured Particle Sizes and $\Delta D_p$ Values at Different Inlet NO$_2$ Mixing Ratios of 200, 400, and 600 ppm |
|-----------------------------------------------|------------------|------------------|------------------|------------------|------------------|</p>
<table>
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<th>set-point temperature (°C)</th>
<th>(a) N$_2$ (zero NO$_2$)</th>
<th>(b) 200 ppm NO$_2$</th>
<th>(c) 400 ppm NO$_2$</th>
<th>(d) 600 ppm NO$_2$</th>
<th>(a – b) $\Delta D_p$ 200 ppm NO$_2$</th>
<th>(a – c) $\Delta D_p$ 400 ppm NO$_2$</th>
<th>(a – d) $\Delta D_p$ 600 ppm NO$_2$</th>
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| TABLE 2. Fitted Kinetic Parameters for Soot Oxidation with NO$_2$ |
|-----------------------------|------------------|
| parameter | value |
| $A_{\text{soot}}$ (nm K$^{-0.5}$ s$^{-1}$ cm$^2$ molecule$^{-1}$) | $2.4 \times 10^{-14}$ |
| $E_{\text{soot}}$ (kJ mol$^{-1}$) | 47.1 |
Table 1 in Choo et al. (15). NO₂ decomposition within their furnace is calculated using $A_{\text{NO}_2}$ and $E_{\text{soot}}$ values in this study. The nonoxidative component of $\Delta D_p$ measured by Choo et al. (15) under zero NO₂ mixing ratio is subtracted from $\Delta D_p$ measured under the presence of NO₂. Fitting is done in a manner as described in section 3 of this study using 2 parameters $A_{\text{soot}}$ and $E_{\text{soot}}$ to fit nine data points. Assuming a reaction order of unity, the fits to data from Choo et al. (15) result in an $E_{\text{soot}}$ value of 45.7 kJ mol⁻¹. This value is significantly lower than value of 76.3 kJ mol⁻¹ reported by Choo et al. (15) but very close to the value obtained by our study (47.1 kJ mol⁻¹). Choo et al. (15) overestimated the $E_{\text{soot}}$ value by a factor of about 1.7, and this error is mainly attributed to neglecting NO₂ decomposition and error in analysis of their data. Lee et al. (19) investigated oxidation of Printex-U carbon black soot with NO₂ using a flow reactor system designed to simulate conditions on a diesel particulate filter. Lee et al. (19) derived an apparent activation energy of 60 ± 3 kJ mol⁻¹ in the temperature range of 250–500 °C for oxidation with NO₂. We examined soot oxidation at a higher temperature range 500–950 °C compared to Lee et al. (19). This temperature range most likely represents temperature conditions during expansion stroke of diesel engines (23) and at the high temperature end for diesel particulate filter (DPF) regeneration. Lee et al. (19) and Kamm et al. (12) also suggested the soot reaction order of 1 with NO₂. If we let the reaction order as a third adjustable parameter in addition to $A_{\text{soot}}$ and $E_{\text{soot}}$ during the fitting, then a value of $n = 0.68$ and an $E_{\text{soot}}$ value of 41.9 kJ mol⁻¹ is obtained from the best fit. However, the reaction order is best determined from plots of $\Delta D_p$ versus NO₂ partial pressures in the furnace as suggested by Nienow et al. (5). In the present study, it is difficult to determine the reaction order with respect to NO₂ as NO₂ mixing ratios change because of thermal decomposition within the furnace.

The current activation energy for soot oxidation with NO₂ is lower as compared to soot oxidation with air. For example, Higgins et al. (3) found activation energy of 164 kJ mol⁻¹ while Lee et al. (19) derived 177 ± 1 kJ mol⁻¹ for soot oxidation with O₂. Our results are consistent with other studies showing significantly lower activation energy with NO₂ oxidation as compared to O₂ (3, 19).

Figure 5 compares current oxidation rates derived from $A_{\text{soot}}$ and $E_{\text{soot}}$ values in Table 2 at different NO₂ mixing ratios, and soot oxidation rate in the presence of air derived by Higgins et al. (3). A density of 1800 kg m⁻³ is used for calculation of surface specific oxidation rate from diameter decrease rate following Higgins et al. (3). The surface specific soot oxidation rate with NO₂ is comparable to oxidation rate with air in the temperature range 800–900 °C. However, air has much higher O₂ mixing ratio (20%), while parts per million levels of NO₂ are sufficient to cause significant soot oxidation. At lower temperatures (below 500 °C), oxidation with NO₂ is expected to be higher than O₂. Experiments for lower temperature range measurement using HTO-TDMA method is a subject for further study. Further studies should also be directed toward understanding soot oxidation rates in presence of other oxidants, such as O₂ and H₂O₂ in addition to NO₂. These studies would help in designing improved soot emission control technologies both in-cylinder and at after-treatment systems such as the diesel particulate filter.

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**Literature Cited**


