Oxidation-derived maturing process of soot, dependent on O₂-NO₂ mixtures and temperatures

Heeje Seong and Seungmok Choi*

Transportation Technology R&D Center, Argonne National Laboratory, 9700 South Cass
Avenue, Argonne, Illinois 60439, U.S.A.

*Corresponding author. Tel: +1 630 252-9239. E-mail: hseong@anl.gov (Hee Je Seong)

Abstract

Oxidizer- and temperature--dependent soot properties was investigated to better understand soot oxidation process. For this work, partially oxidized Printex-U samples as surrogate soot, under three different O_2 - NO_2 mixtures, were analyzed by using the high resolution-transmission electron microscope, Raman microscope and Fourier transform infrared spectroscopy- attenuated total reflectance. The results show that the maturing process was much dependent on NO_2 content in the O_2 - NO_2 mixture: with no NO_2 added, soot oxidized through the internal-burning out process, whereas with increased NO_2 in the mixture, soot tended to oxidize through the external burning process. As the NO_2 content increased, the preferential oxidation of less-ordered carbon crystallites decreased and as a result the maturing process was delayed. Internal burning-out process by O_2 only was also verified at various temperatures and with actual engine soot such as diesel soot and gasoline direct-injection (GDI) soot by TEM observations. Despite similar internal burning-out process, however, it was shown that oxidation at increased temperature resulted in relatively less-ordered soot, implying that soot maturing process was delayed with temperature. Since soot oxidation rate increased with temperature, the increase in oxidation temperature seems to diminish preference on short-ranged crystallites like more efficient O_2 - NO_2 cases.

1. Introduction

Stringent particulate matter (PM) emissions standards have mandated installations of diesel particulate filters (DPF) in diesel engines. Moreover, gasoline particulate filters (GPF) have been developed for targeting the reduction of PM emissions from gasoline direct-injection (GDI) engines. Although detailed regeneration strategies of DPF and GPF systems are ruled by operating temperatures, available oxidizing agents (O_2 and NO_2) and other factors, both systems require soot oxidation through regeneration process to decrease pressure drop across filters because increased pressure drop deteriorates fuel economy.

Soot oxidation accompanies drastic changes in physical and chemical properties of soot. Surface oxygen complexes (SOCs), which are also called surface oxygen functional groups, are created during the reactions of carbon and oxidizing agents and they are subsequently converted into CO and CO_2 by the reactions of SOCs and oxidizing agents [1]. In the meantime, carbon crystalline structure becomes more ordered because less-ordered carbon structures, such as amorphous and short-ranged disordered carbons, are selectively consumed. As excellently summarized by Vander Wal and coworkers [2], the preferential oxidation of those less-ordered carbon at interstitial, non- sp^2 edge sites allows reorganization of remaining crystallites to grow by bonding process between neighboring crystallites. Correspondingly, Hurt et al. described that oxidation reaction, processed by breaking bonds and removing carbon atoms as well as cross links, promotes graphitization through atomic rearrangement [3]. As a result, there observed a significant increase in surface area up to a certain degree of oxidation [4-6], because volatilization of adsorbed compounds allows the access of oxidizers into internal pores, facilitating opening of closed pores with preferential oxidation of less-ordered parts [5,7]. Indeed,

soot graphitization during oxidation was evident by many studies using Raman spectroscopy [8-10], X-ray diffraction (XRD) [11,12] and transmission electron microscopy (TEM) [2,8,11,12].

Initial nanostructure of soot is crucial in determining soot oxidative reactivity [13-14] and many studies confirmed that combustion condition and fuel type had significant influences on structural changes during oxidation. For instance, biodiesel soot [11] and soot generated by a spark discharge aerosol generator [8,9] were found to exhibit drastic changes in nanostructure during oxidation, in comparison to fischer-Tropsch soot and diesel soot, respectively.

Inhomogeneous nanostructural changes of soot trapped in DPF were presumed to be due to soot particles initially formed at different operating stages [2]. Indeed, aggregate particles consisting of primary particles and volatiles showed size-dependent oxidative reactivity, because different sizes of aggregate particles had different volatility, primary particle size and structure order even at the same operating condition [15]. In addition, oxidation conditions play a significant role in oxidation process. Based on the surface area evolution and kinetic model, Strzelec et al. suggested that NO_2 progresses exterior surface oxidation, whereas O_2 does internal burning-out oxidation [16].

Based on previous studies, the current work was conducted to examine soot maturing process of soot under mild oxidation conditions, dependent on oxidizing conditions. Partially oxidized soot samples were prepared under O_2 only and $\text{O}_2\text{-NO}_2$ mixtures. After then, their apparent nanostructures, crystalline structures and SOC were analyzed to better understand oxidation process influenced by oxidizing conditions.

2. Experimental

2.1 Sample preparation

Printex-U (PU) from Degussa AG was used in this work to represent engine soot. Although this surrogate soot has low contents of volatile compounds and ash [17,18], compared with engine soot, our other studies showed that the former has crystalline structure almost identical to GDI soot. Its partially oxidized samples were prepared in a Thermogravimetric analyzer (TGA) as below. In addition, partially oxidized engine soot samples were also prepared in the TGA like PU samples. GDI soot was collected on Teflon filters from a 2.4L production GDI engine, operated at 1500 rpm – 50% load condition, while diesel soot was collected from a single cylinder heavy-duty diesel engine, operated at 1500 rpm – 50% load condition.

2.2 Analysis Tools

Soot oxidation patterns and oxidized samples were examined in a TGA, which is a Q50 thermogravimetric analyzer from TA Instruments. Each sample of approximately 3- 6 mg was placed in a thin-type platinum sample cup (9.85mm (D) x 1.68mm (H)) and it was heated under N_2 gas NO_2 and N_2 mixtures for targeted O_2 and NO_2 concentrations: 8% O_2 in N_2 , 8% O_2 -1000ppm NO_2 in N_2 and 8% O_2 -2500ppm NO_2 in N_2 . The remaining soot mass was instantaneously measured until soot oxidation was completed. Based on these results, the partially oxidized samples at 33, 67 and 90 mass % conversions were obtained under designed oxidizer mixtures.

Raman spectra were obtained on a Renishaw Raman Microscope (In Via) for various oxidized soot samples. A 50X objective lens of the microscope was used to focus and collect spectra using 785 nm (near-IR laser source) in a Raman shift range of 800 to 2000 cm^{-1} with accumulations of 2 times for 100 seconds. To avoid degradation of samples, the incident laser power on samples was performed at 0.5% of full power. The spectra were curve-fitted via IGOR Pro 6.22A

software (Wavemetrics Inc.), where 3 Lorentzian-shaped G ($\sim 1580\text{ cm}^{-1}$), D1 ($\sim 1360\text{ cm}^{-1}$) and D4 ($\sim 1180\text{ cm}^{-1}$), and 1 Gaussian-shaped D3 ($\sim 1500\text{ cm}^{-1}$) were obtained with a linear baseline. The ratio of D3 area to G area (A_{D3}/A_G), D1 full width at half maximum (D1 FWHM) and the ratio of D1 area to G area (A_{D1}/A_G) were used as Raman parameters to determine the order of the carbon crystalline structure, based on previous studies [8-10].

Surface functionalities of soot samples were examined for oxidized samples using Fourier Transform Infrared (FTIR). FTIR spectra were obtained in a wavenumber range of 600 to 4000 cm^{-1} , using a Bruker Vertex 70 spectrometer equipped with a PIKE Technologies MIRacle attenuated total reflectance (ATR). The spectra of each sample loaded in a ZeSe crystal were averaged over 32 scans with 1 cm^{-1} resolution.

Apparent nanostructures were examined for oxidized samples using a JEOL JEM-2100F TEM. Approximately 0.5 mg of each sample and 5 cc of acetone were delivered into a vial and they were sonicated in a sonicating bath for 30 – 60 min until the sample was completely dispersed. One drop of dispersed solution was delivered onto a lacey-carbon TEM grid. The images were taken at the magnifications between 100kX and 600kX.

3. Results and discussion

3.1 TGA isothermal tests of soot

The promoting effect of NO_2 addition on soot oxidation was examined at 500°C . When O_2 concentration was kept constant at 8%, the increase in NO_2 content dramatically enhanced soot oxidation, as shown in Fig. 1: the complete oxidation was realized at 1500, 450 and 230 minutes, when NO_2 concentration increased from 0 to 1000 to 2500 ppm, respectively. Based on Fig. 1a,

instantaneous soot oxidation rates were also calculated as the reaction rate (dm/dt) per the remaining soot mass (Fig. 1b). The instantaneous oxidation rate with 8% O₂ slightly increased over the conversion range of 1 to 98%. With the addition of NO₂, the increase in the oxidation rate was considerable from the initial oxidation stage and it steeply increased with conversion. According to Tighe et al. [19], $k_v(C_{NO_2})^n$, where k_v is a rate constant based on volume of particle, increased linearly with NO₂ concentration for various temperatures. It is obvious that increased NO₂ availability favored the formation of intermediate species from soot and O₂-NO₂ mixtures and eventually accelerated conversion rates from intermediate species into CO and CO₂ [1].

Fig. 1. TGA results of PU samples under different O₂-NO₂ mixtures: (a) Isothermal oxidation at 500 °C, (b) Instantaneous oxidation rate.

3.2 TEM observations of partially oxidized soot

In order to examine changes in physicochemical property during oxidation, partially oxidized samples at 33, 67 and 90% degrees of oxidation were prepared under three different O₂-NO₂

mixtures. Fig. 2 shows representative TEM images of aggregate particles photographed at the magnification of 100,000X. It is apparent that the O₂ only and O₂-NO₂ mixtures manifested different oxidation processes. Similarly, there were no internal voids observed at the early stage of oxidation (33% oxidation) under these different oxidizing mixtures. With 8% O₂ oxidation, however, there found internal voids within primary particles at 67% oxidation and the degree of internal burning was more obvious at 90% oxidation. More than 500 primary particles at each oxidation degree were examined from TEM images to inform how many particles were internally burned: no particles had internal voids for 33% oxidized samples, while around 50 – 70% particles and almost all the particles had voids for 67% oxidized samples and 90% oxidized samples, respectively. Compared to the O₂ only oxidation, with the 8% O₂-1000 ppm NO₂ mixture, internal burning was not observed up to 67% oxidation. However, hollow particles were found to be approximately 30 – 50% for 90% oxidized samples, although the void level is not appreciable. On the contrary, with the higher NO₂ addition of 2500 ppm, no void particles were observed even with 90% oxidation. Consequently, it is obvious that O₂ only preferred internal burning-out process, whereas O₂-NO₂ mixtures did external burning process. The contrasting impacts of different oxidizers on burning process are similar to those of different oxidizing pressures in TGA [20]. Jaramillo et al. showed that a high-pressure oxidizing condition providing a highly reactive oxidizing environment favored external burning process for carbon black (Regal 250) and diesel soot, while an atmospheric condition did internal burning-out process.

Fig. 2. TEM images of partially oxidized PU samples at 33, 67 and 90% degrees of oxidation under three different oxidizing conditions (100,000X) (Fig. S2 shows enlarged images of samples with voids).

These oxidation patterns dependent on NO_2 present were already proposed from kinetic studies by Strzelec et al. [16]. Also, Vander Wal et al. reported high ratio of shell-like void particles among partially oxidized soot from DPF and TGA experiments [2]. However, it is not clear why they could not find such void particles from partially oxidized PU samples, when mild oxidation with O_2 was performed like this work. Although initial nanostructure is a crucial factor influencing oxidation process [2,11,12], the oxidation process seems to be sensitively impacted by oxidizing environments such as temperature, oxygen content and reactor type. For better observations of structural changes under different oxidizing environments, nanostructures of these samples were further investigated at the higher magnification of 600,000X, as shown in Fig. 3. Non-oxidized soot has turbostratic patterns that fringe layers surround nucleus concentrically. The outer surface of primary particle is found to be smooth at this condition. In comparison, the oxidized samples show different patterns, depending on oxidizing mixtures. Internally burned-out samples such as 90% O_2 -oxidized soot contained no noticeable fringe patterns on the center, because less-ordered nuclei were preferentially oxidized by diffused oxygen into porous particles [7,21]. The outermost layers of those particles were characterized with surface roughness of uneven fringes, compared with those of no-void particles like 90%-oxidized soot under 2500 ppm NO_2 addition. As Strzelec et al. explained [16], these divot-like structures could represent pore opening process by selective oxidation. However, we could not find any crumbling structures with NO_2 oxidation like their finding, possibly because they used a much higher NO_2 concentration of 1%. The 90%-oxidized soot by 2500 ppm NO_2 showed fringe patterns and surface roughness comparable to non-oxidized soot. More details of structural changes will be further discussed in the later page.

Fig. 3. HR-TEM images of original PU sample and partially oxidized PU samples at 67 and 90% degrees of oxidation under three different oxidizing conditions (600,000X) (arrows indicate voids from oxidation).

TEM observations were further performed for partially oxidized samples at different oxidizing conditions with O₂: 8% O₂ at 600°C, 1% O₂ at 600°C, and 8% O₂ at 700°C. Because NO₂ effect was observed to be insignificant at these high temperatures [22], TEM observations were not performed for partially oxidized soot with NO₂ added. Noticeable shell-like structures were also demonstrated at the increased temperatures of 600 and 700°C. In addition, the internal burning-out process was exemplified at a low oxygen concentration of 1%, as shown in Fig. 4b.

Fig. 4. HR-TEM images of 90% oxidized soot at various conditions (100,000X): (a) PU sample, 8% O₂, 600°C, (b) PU sample, 1% O₂, 600°C, (c) PU sample, 8% O₂, 700°C, (d) GDI soot sample, 8% O₂, 500°C, (e) diesel soot sample, 8% O₂, 500°C.

Further investigation with gasoline soot and diesel soot also verified that the internal burning-out process was universal at the current oxidizing conditions, as shown in Figs. 4d and e. Therefore, this work with Printex-U seems to be reasonably applied to overall oxidation process of gasoline and diesel soot, although detailed oxidizing steps might not be exactly identical, because these engine soot samples have own unique physicochemical properties, as Atribak et al. discussed [17].

3.3 Raman analysis of partially oxidized soot

To better understand structural changes with oxidation, carbon crystalline structures of partially oxidized soot were examined by using the Raman microscope in Fig. 5. Two characteristic peaks were observed at $\sim 1360\text{ cm}^{-1}$ (D-peak) $\sim 1580\text{ cm}^{-1}$ (G-peak), which are caused by the breathing motion of sp^2 rings and the bond stretching of all pairs of sp^2 atoms, respectively [23].

Depending on NO_2 concentration, several appreciable changes were noted. The first considerable changes during oxidation were the reductions in the width of the D-peak and the height of the valley between D- and G-peaks, regardless of NO_2 concentration. These characteristics represent that with oxidation, the less-ordered amorphous and disordered carbon crystallites were preferentially oxidized, resulting in more ordered crystallites [9]. The structural changes represented by the maturing process were more significant with O_2 only than with NO_2 -assisted oxidation and became less sensitive with increasing NO_2 . As a consequence, the 90%-oxidized soot was more ordered in the order of $8\% \text{ O}_2 > 1000\text{ ppm NO}_2 \text{ mixture} > 2500\text{ ppm NO}_2$, as shown in Fig. 5d. Since O_2 only preferred internal burning-out process, less-ordered carbon crystallites existing abundantly inside particles were selectively removed during oxidation. As a

result, remaining crystallites were found to be more ordered with O_2 only than with O_2 - NO_2 mixtures. These results confirm that soot underwent milder oxidation with increasing NO_2 , as anticipated from TEM results. When the NO_2 concentration in the oxidizer mixtures is much higher than 2500 ppm, therefore, the structural changes during oxidation are expected to be minor.

Fig. 5. Raman spectra of PU samples with oxidation under different oxidizing mixtures: (a) 8% O_2 , (b) 8% O_2 -1000 ppm NO_2 , (c) 8% O_2 -2500 ppm NO_2 , (d) 90% oxidized soot.

Another observation is that regardless of oxidizing condition, Raman spectra varied significantly at the initial oxidation stage (0 to 33%) especially with no and relatively low NO₂ content, and they became almost unaltered at the late oxidation stage (67 to 90%). Accordingly, it is presumed that the crystallite ordering process progressed up to a certain degree of oxidation and the carbon crystallites were stabilized despite continued oxidation. The stabilized structures at the late oxidation stage may indicate that physical properties such as density and surface area remained invariant with further oxidation, as Kandas et al. [5] and Strzelec et al. [6] observed. It is interesting to note that the Raman spectra of the 90%-oxidized sample with 2500 ppm NO₂ is quite comparable to those of the 33%-oxidized samples with O₂ only/1000 ppm NO₂ addition. Since adsorbed compounds blocking oxidizers from accessing inner parts were removed during oxidation [5], the retarded maturing process by O₂-NO₂ mixture implies slow mass transfer of these molecules into inner pores whether or not NO₂-oxidation is governed by the rate of diffusion [19,24]. Despite the apparent external burning oxidation with 2500 ppm NO₂ addition, therefore, this burning process was not a true shrinking-core oxidation, because the structural change accompanying density change won't occur on particles through the true shrinking-core oxidation. Notwithstanding, the "shrinking-core model" can be conveniently used to depict the difference in oxidation rate pattern with O₂-only and NO₂-assisted oxidation as well represented in [16].

Furthermore, some minor changes in Raman spectra also suggest important structural and chemical changes as soot oxidation progressed. The G-peak position appeared to upshift with oxidation: with O₂ only oxidation from 0 to 90%, it gradually shifted from 1596 cm⁻¹ to 1604 cm⁻¹, whereas with 1000 ppm and 2500 ppm additions, it did from 1596 cm⁻¹ to 1603 cm⁻¹ and from 1596 cm⁻¹ to 1597 cm⁻¹, respectively. In addition, the relative G-peak intensity to D-peak

decreased slightly more with O₂ only than with O₂-NO₂ mixtures. Based on Ferrari and Robertson [22], this result provides another evidence that with oxidation, the ordering process occurred at the Stage 2 from amorphous carbon to nanocrystalline graphite. Although disordered and amorphous carbon crystallites were selectively removed during oxidation, however, the degree of modification is thought to be not significant possibly because soot is close to nanocrystalline graphite structure containing a low content of sp³ structure. Lastly, there was a small hump generated at ~1750 cm⁻¹ with oxidation. The peak intensity is more apparent with O₂ only oxidation than with NO₂ oxidation. Since this peak corresponds to increased SOC's such as C=O group [25], O₂-oxidized soot appeared to contain more SOC's than NO₂-oxidized soot. The increasing trend in SOC's with oxidation was further discussed in the later page.

These Raman spectra were curve-fitted with 3 Lorentzian and 1 Gaussian bands and structural analyses were performed for more details. Raman parameters, i.e., the integrated intensity of D₃ to G peaks (A_{D3}/A_G), D1 FWHM, and the integrated intensity of D₁ to G peaks (A_{D1}/A_G), were analyzed to inform the ordering process. The three Raman parameters turned out to decrease with an increase in degree of oxidation under three oxidizing environments. Moreover, it is apparent that the Raman parameters decreased more rapidly with O₂ only than with NO₂-assisted oxidation, which is consistent with the trends in G-peak position and height. In particular, the decrease in portion of amorphous carbon is the most appreciable with oxidation. The D1 FWHM of the 33% oxidized sample with 2500 ppm NO₂ was almost identical as that of the non-oxidized sample and it gradually decreased with oxidation. These results provide a clear sign that amorphous and disordered carbon crystallites were preferentially oxidized and the overall crystalline structure has developed into more ordered form. Although the apparent Raman spectra of the 67- and 90%-oxidized samples at each oxidizing environment appeared to be

almost identical, the decreased values with 90%-oxidized samples imply that these Raman parameters were sensitive enough to capture minor structural changes. On the contrary, the A_{D1}/A_G of the non-oxidized soot was even smaller than those of the oxidized samples in the initial oxidation stages when the O_2 - NO_2 mixtures were used, which contrasts the increased order of structure with oxidation. Since the D1-peak is influenced by the D₂-peak at $\sim 1200\text{ cm}^{-1}$ and the D₃-peak at $\sim 1500\text{ cm}^{-1}$, the non-oxidized soot containing high ratios of these peaks showed a relatively low value. This also reflects the increased order of carbon structure with oxidation, because the D₂-peak is also related to disordered carbon [26]. On the other hand, a cautious interpretation on the A_{D1}/A_G may be required with curve-fitting methods although it has been successfully applied in previous studies [27,28].

Fig. 6. Raman parameters as a function of degree of oxidation with error bars: (a) integrated intensity ratio of D3 to G, (b) D1 FWHM, and (c) Integrated intensity ratio of D1 to G.

3.4 Surface functionalities of partially oxidized soot

In addition to examinations of structural changes under O_2 only and NO_2 -assisted oxidations, their impacts on the surface chemistry were further investigated for partially oxidized samples at

8% O₂ and 8% O₂-1000 ppm NO₂ conditions, as shown in Fig. 8. The complex spectral distributions were assigned as follows: spectra below 1000 cm⁻¹ correspond to C=C-H out of plane bending, the peak at 1230 cm⁻¹ is related to C-O-C, 1580 cm⁻¹ is C=C stretching in the aromatics (others observed this peak at 1600 to 1620 cm⁻¹), 1700 cm⁻¹ is responsible for carbonyl C=O stretching, and 3100 to 3500 cm⁻¹ is attributed to acetylenic C-H and O-H stretching (including H₂O) [29,30]. Because the peaks at 3100 to 3500 cm⁻¹ are caused mainly by H₂O infrared absorbance, these peaks were excluded from analyses of surface functionalities and crystalline structures performed in this study.

From the figure, it is clear that the peaks at 1230, 1580 and 1700 cm⁻¹ significantly increased with increased degree of oxidation under the both oxidation conditions: O₂ only and NO₂-assisted oxidations produced more surface oxygen functionality such as C-O-C and C=O. In addition, since the absorbance of aromatics becomes stronger, it is understood that carbon crystallites develop into more ordered structures as shown in Raman results. When the effects of two oxidizing conditions were compared, O₂ only produced more C-O-C, C=O and aromatics than NO₂-addition, which is consistent with Raman results. As Setiabudi et al. observed [1], the SOC_s produced from NO₂ adsorption were easily converted into CO and CO₂ in the presence of O₂. As a consequence, the remaining SOC_s with NO₂-addition were found to be lower than with O₂ only.

Fig. 7. FTIR-ATR spectra of oxidized PU samples under two different oxidizing conditions.

As discussed early, the efficient NO_2 -assisted oxidation could oxidize both long-ranged crystallites and short-ranged crystallites less selectively than did the O_2 only oxidation, resulting in the delayed ordering process. Unlike crystallite growth by thermal annealing process at high temperatures [31], the ordering process through mild oxidation is presumed to be achieved by preferential oxidation of less-ordered short-ranged crystallites and rearrangement of remaining crystallites [2,11]. In consideration of limited short-ranged crystallites in soot, the rearrangement of crystallites seems to contribute to the reorganizing process among crystallites. For instance, Song et al. [11] showed from TEM observations and image analysis that fringe layers in biodiesel soot only became larger through the realigning process at an advanced level of oxidation. Since the oxidation temperature performed in the work was relatively low for thermal annealing, this rearranging process may occur through reactions among SOC's located at neighboring crystallites. However, this type of rearranging process may have not occurred in this work. As noticeable differences in fringe length were not observed on internally burned soot,

Jaramillo et al. indicated that the lamella on the particle perimeters were not much ordered with internal burning mode [20].

3.5 Crystallite maturing process at increased temperatures

In the real regeneration processes in GPF or DPF systems, the operating temperatures would be another important factor at influencing the maturing process. Since NO_2 may not be useful at high temperatures over 600°C as mentioned, only O_2 effects were investigated for 90%-oxidized samples at various temperatures, assuming that the carbon structure was fully developed at that high conversion. Fig. 8a shows that although the oxidized samples had similar shell-like structures as shown in Fig. 4, the temperature effect on carbon structure was appreciable: with increasing temperature, the carbon crystallite became less ordered, as represented by the increased intensity of the valley between the D- and G-peaks. As indicated in Fig. 7b, with increasing temperature, soot oxidative reactivity was significantly enhanced. The difference in energy barrier for oxidation between less-ordered carbon and more-ordered carbon is expected to be not significant at increased temperatures, so the maturing process through selective oxidation of short-ranged crystallites is less favored at such high temperatures. In this light, these Raman results support that mild oxidation prefers the maturing process [2]. In order to validate this finding, the effects of lower oxygen content of 1% were also examined. The lower oxygen content provided a milder oxidation environment, leading to greatly decreased oxidation reactivity as shown in Fig. 8b. However, the resultant oxidized soot with 1% O_2 was shown to be slightly less ordered than the soot oxidized with 8% O_2 at the same temperature, but the difference is statistically within an error range according to statistical analysis. As discussed above, when the rearranging process did not occur during oxidation, the remaining 10 mass % of the original sample represents stable long-ranged crystallites survived from oxidation. It is

surprising that despite huge difference in soot oxidation reactivity (Fig. 8b), this reaction difference did not lead to noticeable structural difference. The low availability of oxygen molecules may have delayed formation of intermediate species and subsequent reactions. However, it is not clear whether the low oxygen content can result in the reduced preferential oxidation of less-ordered crystallites due to slow penetration into inner pores like O_2 - NO_2 mixtures. Anyhow, this result shows that although the maturing process is favored in mild oxidation, oxygen content of 1% did not bring appreciable structural change, in comparison to the 8% O_2 case at the given temperature condition.

Fig. 8. (a) Raman spectra of 90% oxidized PU samples at different temperatures and (b) TGA results.

3.6 Effects of maturing process on soot oxidative reactivity and other concerns

The graphitized soot, dependent on oxidizer and temperature, may have several engineering and hazardous aspects to be considered in the real regeneration process of DPF and GPF systems.

Since the available NO_2 is not extremely high in consideration of NO emissions from engines, soot will be matured during regeneration process through O_2 only or low NO_2 -assisted oxidation. When the regeneration process is extended at low operating temperatures, partially oxidized soot will remain in filters without complete oxidation. Since this matured soot with increased order of crystallites will continue to be more matured up to a certain oxidized level, there are concerns that the accumulation of matured soot in filters over time would be challenges in operation [2]. To simulate this situation, the PU samples were oxidized up to 30% and 60% degrees, respectively, and were purged for one hour with N_2 at the same 600°C temperature for each case. And then, these partially oxidized samples were re-oxidized to be compared to the original sample as shown in Fig. 9.

Fig. 9. TGA results of original PU and GDI soot samples and their oxidized samples with 8% O_2 in N_2 at 600°C isothermal condition.

Unexpectedly, the TGA experiments showed that oxidation reactivity increased in the order of 60% > 30% > 0% oxidized samples, although carbon crystalline order gradually increased with oxidation. Carbon oxidative reactivity is in agreement with initial structural order [13], and thermal treatment resulting in structural order was shown to decrease carbon oxidation [32]. In this light, there should be some factors that respond to the increased reactivity of the partially oxidized soot. Oxidation should have had increased SOC_s and porosity as examined above, in comparison with the original soot. Oxygen molecules broke and remove adsorbed compounds, closed pores and cross links that blocked oxidizing molecules from approaching inner pores [3,5], so that the molecules could easily penetrate into inner pores. Although some of SOC_s such as carboxylic acid compounds would be removed with N₂ purge at 600°C, they were expected to be resumed quickly with re-oxidation. As suggested [11], edge sites containing abundant SOC_s would be easy targets for further reactions into CO and CO₂, despite reduced edge sites resulting from increased long-ranged crystallites. Even though carbon crystallites became more ordered with oxidation, the increased level of maturity with mild oxidation might be less significant at affecting soot oxidation reactivity than the increased SOC_s and other factors. Despite this hypothesis, however, Fig. 9 also showed relatively minor effects of oxidation on soot oxidation reactivity in the case of GDI soot. According to our other unpublished work, the increase in crystalline order was also observed for GDI soot during oxidation. Therefore, the minor increase in soot oxidation reactivity with oxidation might be related with uniqueness in GDI soot that contains matrix-bound organic distributed within the particles [33]. Although the degree of improvement in soot oxidation reactivity seems to be impacted by initial soot properties, these results still suggest that matured soot with oxidation may not be as resilient as fresh soot toward oxidation.

Another consideration is the emissions of matured soot from these filter systems, because migrated small nanoparticles can exit large open pores of the filters without accumulation, especially before filter pores are yet to be plugged with ash loading. Because PM emissions from filter systems are low, their effects on health and the environment have not been thoroughly investigated. However, a recent study showed that although the total number of particles deposited in lungs decreased with the installation of DPFs, post-DPF particles were found to contain a variety of elements known to be harmful to humans [34]. In addition, although the nature of small nanoparticles emitted from DPF and GPF systems needs to be further investigated, those particles can be fragmented soot particles escaped during regeneration [35]. If these emitted particles are oxidized soot, they have different physicochemical properties than those of engine-emissions soot; they will contain significantly increased SOC and surface porosity. These reactive nanoparticles can be easily inhaled and absorbed into human bodies when their sizes are sub-100 nm. Therefore, future studies will require detailed examinations of nature of post-filter particles, their physicochemical properties and potential dangers.

4 Conclusions

We investigated the impacts of oxidizers consisting of O_2 and NO_2 in N_2 balance on soot maturing process, based on HR-TEM, Raman microscopy and FTIR-ATR analyses. With no NO_2 present, soot showed clear internal burning-out process represented by shell-like particles with more-ordered crystalline structure containing increased surface oxygen complexes. With increasing NO_2 content, however, the internal burning-out process was retarded and thus there were no shell-like particles observed with an increased NO_2 content. Although it is anticipated

that soot oxidation follows core-shrinking model when NO₂ content is extremely high, the preferential oxidation of less-ordered carbon still occurred on soot particles containing no apparent voids, implying that the true core-shrinking oxidation was not achieved in this examined range of NO₂ content. Because NO₂, which is an active oxidizer when coupled with O₂, preferred external burning oxidation, oxidation of short-ranged disordered crystallites existing inside particles was retarded, resulting in delayed maturing process. Internal burned-out process was observed for soot samples oxidized at different temperatures of 500°C, 600°C and 700°C with O₂ only, but the increase in oxidation temperature tends to delay maturing process. Like O₂-NO₂ cases, the retarded maturing process seems to be related to decreased oxidation selectivity of short-ranged crystallites at increased temperatures.

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