Size distribution and oxidation rate of carbon nanoparticles

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**Diesel engine**
- Advantage of lower fuel consumption
- More particulate matters (PM), human carcinogen
- Stricter exhaust gas emission standards such as Euro VI

**Diesel Particulate Filter (DPF)**
- Wall-flow ceramic filter to trap PM in exhaust after-treatment
- Easily Plugged, need to remove accumulated particles

⇒ Filter regeneration, catalyst to reduce oxidation temp.
- PM is oxidized by catalyst indirectly
- Compared with O₂, NO₂ is much more reactive for soot oxidation
- Quantitative effect of NO₂ on soot oxidation is not clear
Objective

As for promotion of diesel soot oxidation, few data on particle size distribution and number is available

(1) Most of diesel soot is trapped by DPF, and we cannot evaluate variation of soot particle size during oxidation process in CRT system
(2) Characteristics of diesel soot depend on fuel properties, exhaust gas component, engine conditions

By using carbon particle generator, carbon particles are reacted in a temperature-controllable tubular furnace. Oxidation process is analyzed by monitoring particle size and its number concentration.
Experimental Setup

Temperature-controllable tubular furnace

Scanning mobility particle sizer (TSI, SMPS3034)

Gas analyzer (CO, CO2, NOx)

Soot Aerosol Generator

Carbon particle generator (Palas, GFG-1000)
Size Distribution of Carbon Particle

(1) Diesel soot by EEPS (SAE Paper 2011-01-0817, 2011)
(2) Carbon particle by SMPS (present study)

- Both distributions have a single peak, not a double peak
- Size distribution is in the range of 20 nm to 300 nm
- Particle number of diesel soot is slightly larger than that of carbon particle
Experimental Conditions

Experimental conditions

- Temperature:
  200～1100°C

- Gas component:
  Oxygen concentration \( (X_{O_2}) \): 0～20 %
  NO\(_2\) concentration \( (X_{NO_2}) \): 0～2000 ppm

Results

① Size distribution of carbon particles
② Particle diameter
③ Total particle number and volume fraction
④ Reaction rate constant by Arrhenius plot
- Little change is observed in size distribution until temperature is 345 °C.
- At 530 °C, size distribution is only shifted to smaller particle size. No substantial change in number concentration is confirmed.
- At 820 °C, size distribution is largely shifted and mode particle size is reduced by 50%, compared to the original value.
- Even when temperature is 345 °C, a clear difference from the original size distribution is observed.
- Oxidation temperature is reduced in presence of NO₂.
- At 660 °C, size distribution is shifted to a greater extent. At 820 °C, most of particles are oxidized.
- For comparison, experiment of no oxygen was conducted. Reasonably, when there is no oxygen, diameter is not changed.
- Original particle diameter is 105 nm. When oxygen is 10 %, $D_p$ starts to decrease around 400 °C.
- When more NO$_2$ is added, $D_p$ is smaller.
When particles are oxidized, particle size is firstly smaller, with same number
Volume fraction of particles is calculated

\[ f_v = \sum_{i=1}^{u} \frac{\pi}{6} D_{p,i}^3 \cdot N_i \]

- When \( X_{O_2} \) is over 5%, no large difference is observed.
- It implies that, within present conditions, carbon oxidation process would depend only on amount of particle when oxygen is 5% or more.
- Similarly, \( f_v \) decreases as \( T \) is increased, but \( f_v \) is smaller as more NO\(_2\) is added.
- Total number of particles \( (N_T) \) before oxidation is \( 2 \times 10^7 \) 1/cm\(^3\).
- \( N_T \) decreases as \( T \) is increased. In particular, at 820 °C for \( X_{NO_2} = 2000 \) ppm, \( N_T \) is reduced to \( 9.6 \times 10^5 \) 1/cm\(^3\) (3 % of original value).
- \( f_v \) decreases at a lower \( T \), suggesting that, particle size firstly decreases, and then, particle number decreases due to complete burnout of individual particle.
- For $X_{\text{NO}_2} = 0$ pm, $k$ is close to that of diesel soot without catalyst.

- When NO$_2$ is added, at temperature below 650 °C, $k$ for $X_{\text{NO}_2} = 1000$ pm is close to the value of diesel soot without catalysis. At high temperature of 700 to 800 °C, $k$ for $X_{\text{NO}_2} = 2000$ pm is close to the value with catalyst.
Summary

We used carbon particles as model soot, and carbon particle size and its number concentration were experimentally measured. To realize oxidation at uniform temperature, a tubular furnace was used. Following results were obtained.

(1) Carbon particle size and number concentration decrease as furnace temperature is increased. When only oxygen is an oxidizer, little change is observed in particle size distribution until temperature is 345 °C. Carbon particle starts to be oxidized at 420 °C. Hence, the bulk particle size firstly decreases, and then, the particle number becomes smaller.

(2) When NO$_2$ is added, oxidation temperature is reduced. Roughly, in the presence of NO$_2$, carbon oxidation rate is close to the value of diesel soot with catalyst.