Mechanistic Study on Generation and Growth of Ash Particles from Lubricant Additives

Junya ONODA[1], Akira ODA[1], Atsushi SATSUMA[1]
[1]*Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan.*

Significance and Relevance
The generation and growth mechanism of ash particles from lubricant additives was investigated from a molecular and microscopic point of view. TG-DTA results clarified the stepwise decomposition of calcium sulfonate and magnesium sulfonate, while ZnDTP decomposition proceeds only in one step. Although pure calcium ash forms small ash particles with a relatively uniform size distribution, Zn-containing ash forms large sphere particles around 1000 nm because of the role of Zn as a binder of ash particles
Preferred for the topic: Automotive and stationary emission control, Air cleaning and combustion
Preferred presentation: Poster

Introduction
Clean diesel vehicles are equipped with a particulate filter (DPF: Diesel Particulate Filter). Accumulation of ash in the DPF is one of the serious problems,[1-3] therefore, the effects of ash accumulation have been investigated mainly on DPF pressure drop, pumping losses, and increase in regeneration frequency, and so on.[4-6] The present study focused on the chemistry of ash generation from additive molecules and the growth of ash particles.

Experimental
Calcium sulfonate (TBN=400), Magnesium sulfonate (TBN=400), and Zinc dialkyldithiophosphate (ZnDTP) were supplied as a diluted solution in a base oil. TG-DTA profiles were measured with Rigaku TG8121 thermogravimeter in a flow of 0-20% O_2/N_2 (100 mL min^{-1}) at a heating rate of 5 °C min^{-1}. To observe the particle growth of Ca-derived ash particles, a model PM (particulate matter) was prepared by impregnation of an aqueous solution of $(CH_3COO)_2Ca\cdot H_2O$ to model carbon (Printex V), followed by evaporation at 60 °C, dryness overnight at 80°C, and calcination in pure N_2 at 500°C for 3 h.

Results and Discussion
1. Decomposition of Oil Additives to Ash

Thermal decomposition of additives was evaluated by TG-DTA. As shown in Figure 1, the weight of the diluted calcium sulfonate decreased stepwise. The residual weight of zero means that the diluted additives are completely converted to inorganic ash such as $CaCO_3$ and $CaSO_4$. The oxygen concentration did not much affect the decomposition temperature. From the weight ratio and heat generation, the stepwise decomposition can be assigned to (1) partial oxidation and subsequent removal of the side chain around 300 °C, (2) oxidation or removal of aromatic rings at 400-500 °C, and (3) removal of SO_2 at 700-800°C (Figure 2). The rate of weight loss at 300-400°C was sensitive to both the oxygen concentration and temperature ramp rate, however, the inflection temperatures were not affected. Similar profiles were observed for the decomposition of magnesium sulfonate. As for ZnDTP, only a rapid weight loss at around 280 °C was observed.

2. Growth of Ash Particles

The states of residual components in an oxygen-containing atmosphere were analyzed by XRD and Raman. In Raman spectra, the G-band and D-band of soot derived from organic parts of additives were observed below 700 °C, and the bands disappeared after heating at 800 °C. The crystalline size of inorganic compounds was estimated from XRD patterns and shown in Figure 3 as a function of temperature. Only $CaCO_3$ was observed below 600 °C, while $CaSO_4$, and CaO were also formed above 600 °C, indicating decomposition of $CaCO_3$ into CaO and sulfation of $CaCO_3$ and/or CaO at higher temperatures. Although the crystalline size from XRD was below 40 nm, the particle size distribution of ash analyzed by Laser diffraction was around 200-1000 nm. The results mean that the ash particles are composed of agglomerated small primary ash particles to form secondary particles.

The state of the secondary particles was measured with STEM-EDX using the model PM ($CaCO_3$ supported on carbon black). After heat-treated at 700-900 °C in 10% O_2, agglomerated cubic crystals of $CaCO_3$ were observed. Their sizes were in a relatively narrow range around 50 to 100 nm. When the model PM and a residual of heat-treated ZnDTP at 500 °C were mixed (Ca/Zn = 1:1) and heated at 700 °C for 3 h in 10% O_2, very large sphere particles around 1000 nm were observed. The chemical analysis by EDX revealed that Zn is concentrated in the sphere particles. Considering the low melting point of Zn metal at 419 °C, the role of Zn metal in the formation of the large sphere particles can be speculated.

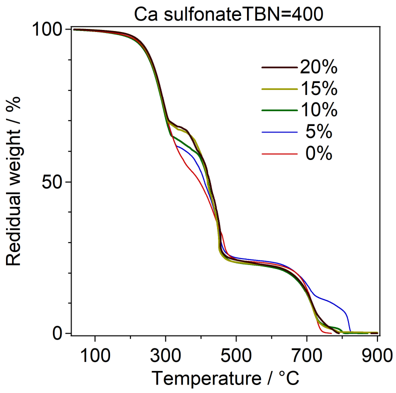

Figure 1. TG profiles of calcium sulfonate decomposition under various partial O_2 concentrations.

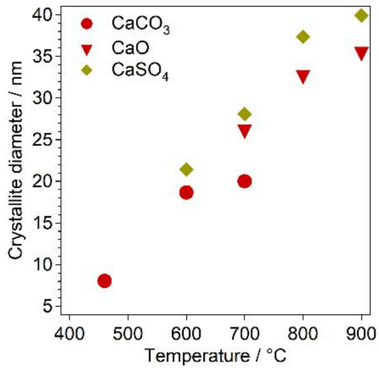

Figure 3. Temperature dependence of crystalline diameter of calcium sulfonate derived ash.

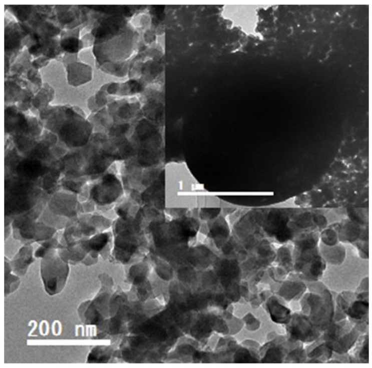

Figure 4. TEM images of ash derived from calcination of $CaCO_3$/C and ZnDTP mixture at 700 °C for 3 h.

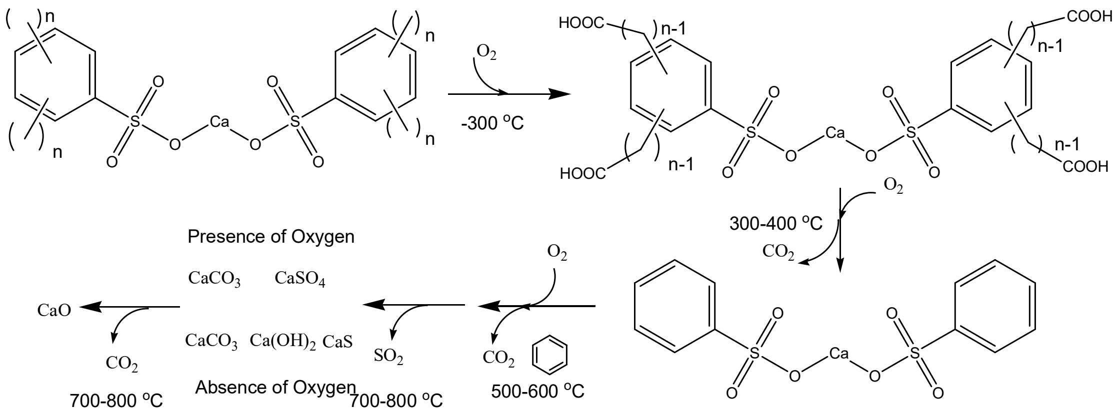

Figure 2. Schematic scheme of calcium sulfonate decomposition into ash.

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Acknowledgments

This work is the result of the research project with The Research association of Automotive Internal Combustion Engines (AICE). The authors gratefully acknowledge the concerned personnel. The authors thank Dr. Yuta Yamamoto, Institute of Materials and Systems for Sustainability, Nagoya University, for their contribution to STEM-EDX measurements.