

De-Ash Characteristics using a Cleaning Agent KOH of CDPF for PM Reduction of Diesel Engines

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Abstract: The objective of this study is to investigate the physicochemical properties of the catalysts and the feasibility of remanufacturing them after removing ash in CDPF using a cleaning agent KOH. Compared with the carbon oxidation ability of fresh CDPF, that of de-ashed CDPF had an insignificant difference due to the low activation energy of CO and CO₂. As ash deposited in CDPF was de-ashed with KOH, it had a practical feasibility on remanufacturing point of view, but washcoat was melted about 26%. Further studies were required for the prevention of washcoat loss.

Key Words : Diesel engine, PM, NO_x, CDPF, Ash, Catalyst

1. 서 론

The emission regulations are recently becoming more stringent due to exhaust toxic gas that is emitted from vehicles, ships, and agricultural machines.¹⁾ The costs of catalytic emission controls that are installed to satisfy those regulations are expensive as they consist of precious metals.²⁾ Depending on the combustion characteristics, the mechanisms vary; however, the reality is that particulate matters are produced in large quantities during the diffusion combustion of diesel engine, so DPFs (Diesel Particulate Filter) are installed to reduce them.³⁻⁵⁾

In addition to trapping the PM, the filter also trap metal oxide "ash"⁶⁻¹⁰⁾ that are carried by the exhaust gas. The ash materials are not combustible and removed during regeneration, thereby, are

accumulated in the DPF. Recently, PM emission needs to be oxidized or removed physically from the DPF system. In the oxidation method, inorganic oxide materials are added into the diesel fuel as additives admixture to remove the accumulated PM. However, the physical removal method is hardly used because of its ineffectiveness.¹¹⁾ Inorganics oxide materials of sulfates, phosphates, or other oxides of calcium and zinc are formed in the engine's combustion chamber from burning of additives in the engine lubrication oil. Some oxides of metal such as iron, manganese and cerium, which are presented as additives to the diesel fuel to achieve a lower oxidation temperature, are required to initiate combustion of the soot in the DPF during regeneration.¹²⁾ Table 1 shows the Reported ash components properties.¹³⁾

Recently, CDPF(Catalytic Diesel Particulate Filter) are utilized to increase the oxidative ability of PM in lower temperatures. If ash has been deposited that a filter has lost its function after the burning of fuel or engine oil, the filter needs to be

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replaced with new one, which increases the cost burden. If ash could be removed periodically that catalysts are re-used rather than replaced, the replacement costs for CDPF that are installed in vehicles, ships, and agricultural machineries could be reduced. It would lead to a great economical gain and is academically meaningful as well.

The objective of this study is to investigate the physicochemical properties of the catalysts and the feasibility of remanufacturing them after removing ash from CDPF with KOH that is strongly alkaline and has a high degree of ionization.

Table 1 Reported ash components properties

Chemical Formula	Melting Point(°C)
CaSO ₄	1,460
MgO	2,832
MgSO ₄	1,124
ZnO	1,975
Zn ₃ (PO ₄) ₂	900

2. Experimental setup and method

2.1 Catalyst preparation and de-ash treatment

To collect samples, ash was scraped from intake manifold that connects to EGR valve of an actual diesel vehicle that has a mileage of 150,000km since it is difficult to make the ash samples. The ash was then dissolved in diesel, and 1.5g was loaded into AT-CDPF (Pt/Pd/Rh, 2/1/0, g/L). It was then dried in oven at 80°C for 24 hours. The CDPF with ash deposits was put in 50cc KOH(KOH:100g, water: 600g), which is strongly alkaline and has a pH of 10, and it underwent the de-ash process by the vibrations of ultrasonic cleaner at 40°C for 4 hours based on previous research experience. Then, the de-ash CDPF was washed three times with ethanol and three times with water. It underwent(2L/min) flushing for 30 minutes at the catalytic temperature of 600°C and

10% O₂, and then the exhaust gas conversions were measured.

After the de-ash process, the experimental equipment for model gas reaction were used to assess the exhaust gas reduction of catalyst. Also, De-PM performance of de-ash CDPF with loaded Printex-U(2g/L) was evaluated.

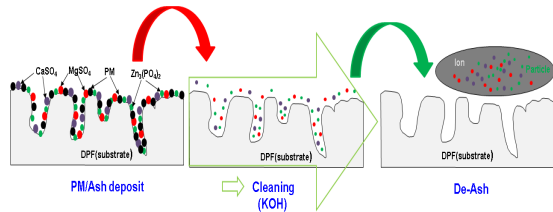


Fig. 1 The proposed de-ash mechanism using KOH

Fig. 1 shows the proposed de-ash mechanism using a cleaning agent KOH. Fig. 2 shows the pictures of fresh and de-ash CDPF samples. Even though some ash remains on the edges of de-ash CDPF, the pictures show the ash being flushed with KOH and removed. The size and size distributions of the particles on CDPF sample surface were observed by transmission electron microscopy(TEM, JEM-2000FXII(200 kV), JEOL) equipped with an energy dispersive X-ray(EDX) detector.

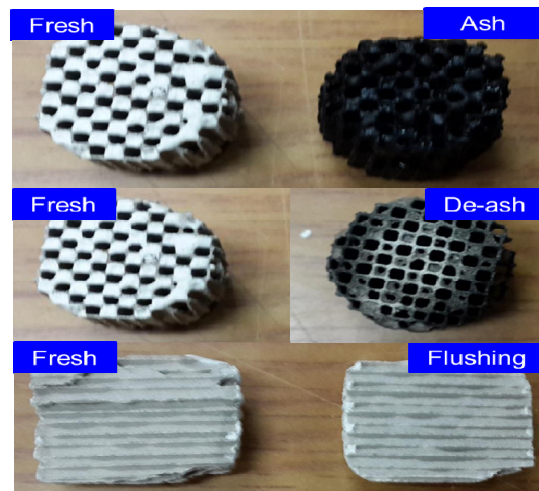


Fig. 2 Photo according to fresh and de-ash CDPF

2.2 Experimental apparatus and evaluation

Catalytic tests of CDPF were performed using the monolithic type in a fixed-bed-flow reactor system. It was composed of a gas-supply component, a catalyst reaction component, an analyzer, and a control device. The total flow rate of the model gas was 2 L/min. The water content was adjusted to 1.5% by the saturated water vapor pressure. The catalyst temperature was measured by fixing a K-type thermocouple($\phi=0.5\text{mm}$) at the center of the catalyst bed. The gas composition after the catalytic reaction was measured at intervals of 5 seconds using an FTIR(Midac, I2000). Fig. 3 shows the schematic of model gas catalytic reaction equipment. The harmful gas conversion ratio of the CDPF was investigated at catalyst temperatures in the range 120–500°C in the transient mode, at a heating rate of 10°C/min. The conversion ratio was calculated using Eq. (1).

$$\text{Conversion (\%)} = (\text{Gases}_{in} - \text{Gases}_{out}) / \text{Gases}_{in} \times 100 \quad (1)$$

In Eq. (1), Gases_{in} and Gases_{out} are the gas concentrations at the inlet and outlet of the catalyst, respectively.

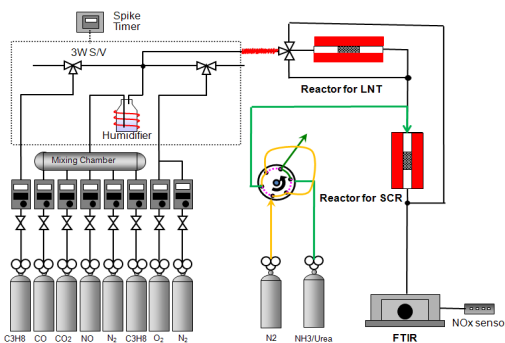


Fig. 3 Schematic of model gas catalytic reaction equipment

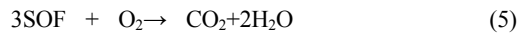
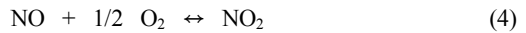
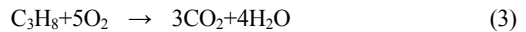
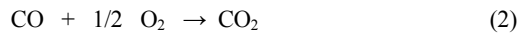
Table 2 shows the experimental conditions for evaluating de-ash performance.

Table 1 Experimental conditions for evaluating de-ash performance

Gas components	Composition
CO(ppm)	700
C ₃ H ₈ (ppm)	150
NO(ppm)	500
O ₂ (%)	10
H ₂ O(%)	1.5
SV(h ⁻¹)	31,454

3. Experimental results and discussion

The harmful gases emitted from a diesel vehicle include CO, HC, NO_x, SOF and PAH. This study only considered CO, HC, and NO.



Equations (2)-(5) show the oxidation reaction equations for harmful gases; the activation energies of the products differ depending on the gases. CO produces CO₂ with the least activation energy(407MJ/kmol), compared to other gases¹⁴.

Fig. 4 shows the exhaust gas conversions after de-ash treatment. As CO gas has a low activation energy, the difference between exhaust gas conversions of fresh and de-ash CDPF samples were not significant. In the case of C₃H₈(2110MJ/kmol), which is stable as type of paraffin, the conversions for fresh catalyst reaches LOT 50 at 355°C and up to 100% at 460°C. However, the sample that has undergone the 4 hours of de-ash process with strongly alkaline KOH displayed only 12% conversion at 500°C. In the

case of NO, being produced in large amounts at high combustion temperatures, fresh catalyst showed 55% of conversion, which is the highest, at approximately 290°C. De-ash CDPF samples had the highest conversion of 31% at approximately 410°C, and the conversion window moves to the right side, and the reaction rate is slow.

The oxidation reactions for harmful gas occur in the following orders : CO, NO, and HC. For gas with a strong bonding structure, the reduction in exhaust gas conversion is great for catalysts that has undergone de-ash process. This is due to the large activation energy that is required for the cracking of exhaust gas and also causes washcoat loss.

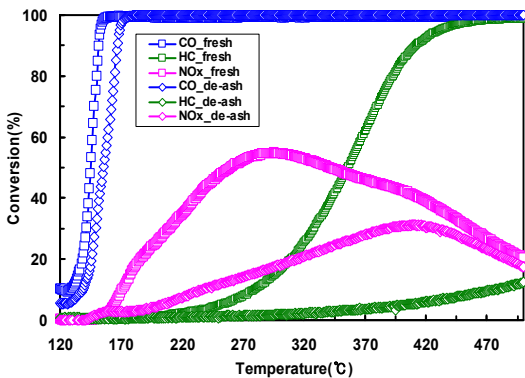


Fig. 4 Exhaust gas conversion after de-ash treatment(4h)

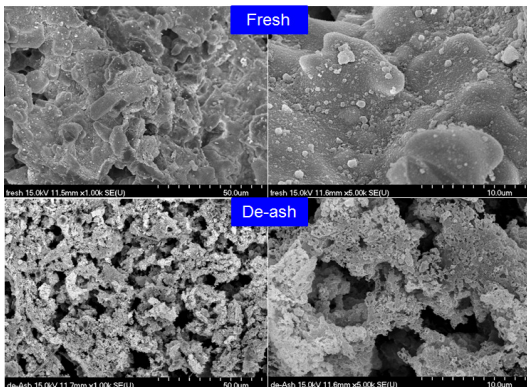


Fig. 5 SEM image after de-ash treatment (4h)

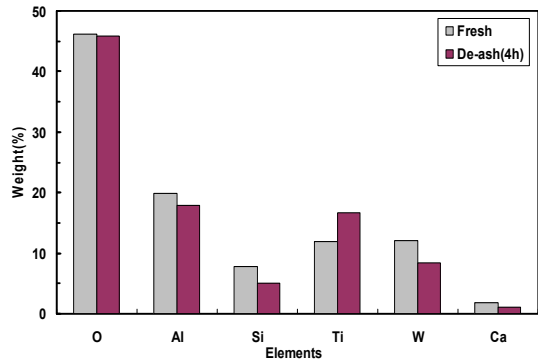


Fig. 6 SEM-EDX after de-ash treatment(4h)

Fig. 5 depicts the SEM images of catalysts after fresh/de-ash treatment. The tendency towards the melting of washcoat stands out for de-ash CDPF, and this is because of the loss of washcoat due to the progression of ionization through the chemical reactions of the catalysts(Pt/Pd) and co-catalysts with strongly alkaline KOH.

Fig. 6 displays the weight of elements of de-ash CDPF's SEM-EDX. As seen in SEM images of Fig. 4, this is due to the melting and loss of a part of the catalysts' washcoat by strongly alkaline KOH.

Fig. 7 shows the weight of fresh and de-ash CDPF. Compared to fresh CDPF, the weight of de-ash CDPF washcoat was decreased by 26%, and the activation of catalysts declined with the reduction of catalysts and additives catalyst.

Fig. 8 shows the oxidation abilities for car bon by loading 2g/L of PM(Carbon) on fresh and de-ash CDPF samples. For fig. 8(a) fresh CDPF, the 2g/L of loading carbon started to be oxidized into CO at 400°C, and into 40ppm of CO and 93ppm of CO₂ with the peak at 600°C. However, for fig. 8(b) de-ash CDPF, C starts to be oxidized at 400°C into CO, which is low in activation energy, but the CO and CO₂ concentrations are reduced by a small margin compared to those of fresh CDPF. It denotes the decrease in oxidation

ability due to the loss of washcoat of catalytic substances by de-ash process.

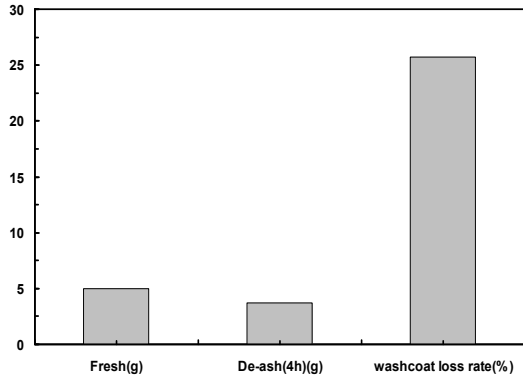
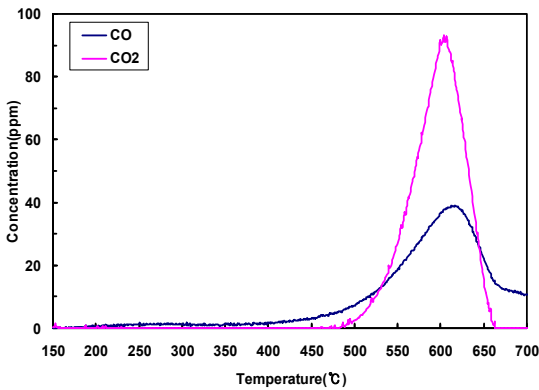
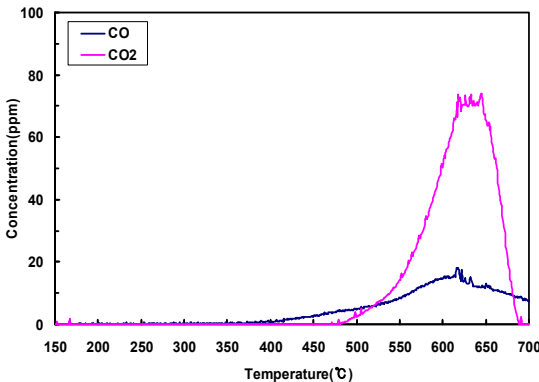


Fig. 7 SEM-EDX after de-ash treatment(4h)



(a) Fresh



(b) De-ash

Fig. 8 De-PM performance after de-ash treatment (4h)

Through this study, ash deposited in CDPF showed a tendency of being washed with KOH, which proves a practical feasibility on remanufacturing point of view. However, further studies on cleaning agents, concentrations of cleaning agent, and cleaning durations are required to prevent the problematic washcoat loss due to de-ash with the strongly alkaline agents.

4. Conclusions

The In this study, the following results were obtained through the physicochemical properties and the feasibility of remanufacturing them after removing ash from CDPF with KOH.

The exhaust toxic gas was oxidized in the following orders : CO, NO, and C₃H₈. For gas that has a strong bonding structure and requires a great activation energy, the exhaust gas conversion of de-ash CDPF decreased.

Compared with the carbon oxidation ability of fresh CDPF, that of fresh CDPF, the oxidation ability of de-ash CDPF for carbon had an insignificant difference due to the low activation energy of CO and CO₂.

The weight of de-ash CDPF washcoat was decreased by 26%, and the activation of catalysts declined with the reduction of catalysts and additives catalyst.

4. As ash deposited in CDPF was de-ashed with KOH, it had a practical feasibility on remanufacturing point of view. However, further studies were required for the prevention of washcoat loss.

Acknowledgement

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