Catalytic Performance Degradation Characteristics and Characterization of CDPF in Laboratory Hydrothermal Aging and Diesel Vehicle Durability Aging

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Abstract. As emissions regulations become increasingly stringent in recent years, the Durability of DPF become more and more important. In this paper, Catalytic performance degradation characteristics of CDPF applied on diesel vehicle durability aging (CDPF was carried out sixty-thousand-kilometer durable ageing) and laboratory hydrothermal aging were studied. The aging of the DPF was analyzed by XRD/XPS sample characterization and sample activity evaluation. The results showed that the crystallinity of diesel vehicle durability CDPF (Used), were higher than that of fresh samples (Fresh) and laboratory aging samples (Aged). The Pt atoms concentration ratio on the surface of Fresh, Aged and Used samples showed a decreasing tendency, which were 1.34%, 0.80% and 0.43% respectively. The concentrations of Pt⁴⁺ in high oxidation state also showed a decreasing trend, which were 0.70%, 0.38% and 0.23% respectively. The Aged and Used samples of CDPF presented oxidative activity degradation on CO and C₃H₈. There was strong correlation between activity degradation and reduced rate of precious metals on the carrier surface.

Introduction

Diesel engine is widely used in transportation, engineering machinery, ships and other power equipment, due to strong power and high fuel economy. In recent years, emission regulations have become increasingly strict, and technologies such as fuel injection control and optimized combustion of diesel engines have gradually made breakthroughs and improvements. However, the internal purification technology of diesel engines alone cannot meet the requirements of emission regulations. To reduce the particulate matter emission of diesel engines, many diesel particulate purification technologies have been developed, including DOC (Diesel Oxidation Catalyst), POC (Particulate Oxidation Catalyst) and DPF (Diesel Particulate Filter), which are the most widely used technologies. Combined with the status quo of research and application, it is currently installed on diesel vehicles by means of DOC and DPF coupling. This technology is simple in packaging, installation, control and maintenance, and has low cost. In terms of emission reduction effects, not only the particulate matter of diesel vehicles is effectively reduced, but also CO, HC and other pollutants in the exhaust gas can be greatly reduced; In the regeneration of DPF, the NO in the diesel exhaust gas is oxidized to NO₂ through the DOC. NO₂ is a strong oxidant, and the carbon dioxide particles trapped in the DPF can be redoxed in the normal temperature range of the diesel engine [1]. In recent years, in order to further promote the combination of DOC and DPF technology to purify diesel exhaust pollutants and achieve better carrier regeneration, catalyst was coated on the surface of DPF carrier (CDPF). On the one hand, the catalyst can be used to remove CO, HC and other pollutants from diesel exhaust. When NO is oxidized to NO₂ by catalytic oxidation of dyes, NO₂ molecules can better contact soot particles in DPF carrier and act as gas catalyst. CDPF has good purification effect on primary and secondary particulate gaseous precursors (CO, HC, etc.) of diesel engine, and can effectively promote the catalytic regeneration of soot trapped by carrier [2].
However, the long-term use of CDPF catalytic performance will be significantly deteriorated, resulting in regeneration performance deterioration, increased emissions and other problems, mainly the exhaust temperature and frequent regeneration of high temperature catalyst will cause high temperature deactivation [3,4]. Fuel and lubricating oil sulfur, phosphorus content will also cause catalyst chemical poisoning. With the increasingly stringent regulations, the durability of post-processing systems is increasingly demanding. The research on DOC supports and catalysts is relatively mature, but there is no systematic study on the deterioration of catalytic performance after laboratory hydrothermal aging and diesel vehicle durability aging. In this paper, the hydrothermal aging of a CDPF in the laboratory and the actual road aging of the whole vehicle are carried out respectively. The relationship between the physical and chemical structure of the surface of the CDPF and its catalytic performance is analyzed by XRD, XPS characterization technology and catalytic activity evaluation system.

**Test Materials and Methods**

**Parameter of CDPF**

The CDPF properties are summarized in Table 1.

| Properties                        | Parameter  |
|-----------------------------------|------------|
| length /mm                        | 305        |
| Diameter /mm                      | 290        |
| Channel density /cpsi             | 200        |
| Porosity /%                       | 55         |
| Pore diameter /μm                 | 8~13       |
| Main material of carrier          | Cordierite |
| coating                           | γ-Al₂O₃ + TiO₂ |
| Composition and proportioning of main catalysts | Pt:Pd:Rh =10:2:1 |
| Main catalyst dosage (/g/ft³)     | 25         |
| Cocatalyst                        | Fe₂O₃ + CeO₂ |
| Cocatalyst dosage (/g/l)          | 20         |

**CDPF Sample Characterization and Activity Evaluation Scheme**

In this paper, D8 ADVANCE X-ray diffractometer of Bruker Corporation was used to detect and analyze the samples of CDPF catalyst, and the phase change, crystallinity and cell parameters of the samples were determined. X-ray diffraction (XRD) can accurately determine the crystal structure, grain size and stress of catalytic samples, and precisely perform phase analysis, qualitative analysis and quantitative analysis [5].

In this paper, PHI 5000C ESCA X-ray photoelectron spectroscopy (XPS) of Perkin Elmer Company was used to analyze the relative content ratio and valence distribution of elements on the surface of catalyst samples. X-ray photoelectron spectroscopy (XPS) is an effective method for the determination of element composition and chemical state on the surface of catalytic materials [6].

In this paper, the activity of small samples of CDPF was evaluated by temperature programmed
method. The activity evaluation device was composed of gas distribution unit, reaction unit and analysis unit, as shown in Fig. 1.

![Diagram of CDPF catalytic activity evaluation system](image)

**Figure 1. The CDPF catalytic activity evaluation system.**

**CDPF Hydrothermal Aging Conditions**

In this paper, a tubular resistance aging furnace was used to treat fresh CDPF samples at high temperature. The gas mixing system of aging furnace can mix various gases and pass the sample. The reaction tube used for placing the sample is high density quartz, which effectively avoids the reaction between the mixed gas and the reaction tube. In addition, a water bubbling system is installed in the resistance furnace to add moisture to the aging process. According to reference [7,8], the hydrothermal aging conditions of the simulated diesel vehicle are designed as follows: temperature is 750°C; duration is 20h; space velocity is 40 000 h⁻¹; gas composition (volume fraction) is 10% O₂, 5% CO₂, 10% H₂O, and N₂ is equilibrium gas. The parameter setting and operation methods of related instruments comply with the standard requirements.

**Experiment Scheme**

In order to study the difference of catalytic performance of CDPF after aging in laboratory conditions and durability of diesel vehicles, fresh samples (Fresh), laboratory aging samples (Aged) and diesel vehicle durability aging samples (Used) were sampled for characterization analysis and activity evaluation. The Used samples were cut at the center of 60,000 km aging sample of diesel vehicle, and then the characterization and activity evaluation of small samples were carried out. XRD was used to analyze the phase structure and crystalline phase parameters of the sample, XPS was used to detect the surface element concentration and valence state of the sample, and gas catalytic activity evaluation system was used to evaluate the activity of the sample.

It should be noted that the Used samples were manually maintained, including soot burning and ash removal, to ensure that the surface of the CDPF carrier is clean, to reduce the impact of soot and ash on test results in characterization analysis and activity evaluation.
Results and Discussion

Analysis of Phase and Cell Parameters

Figure 2. X-ray diffractograms of fresh, aged and used sample of CDPF.

Fig. 2 shows the XRD patterns of fresh, aged and used sample of CDPF. It showed obvious characteristic diffraction peaks in the range of 10-11°, 17-22° and 25-31°. The strong characteristic peaks of each cluster were labeled, followed by a, b and c characteristic peaks, which were magnified and displayed. The characteristic peaks of Fresh, Aged and Used sample shift to large angles in turn, indicating that the cell parameters tend to decrease. Some new crystalline phases appeared in the XRD spectra of Used samples, which may be the poor crystalline phase formed by dispersed precious metals and metal oxides during the aging process, and may reduce the catalytic activity of the catalyst samples.

Table 2. Crystal cell parameters and crystallinity of CDPF samples.

| Samples | cell parameter α(Å) | cell parameter β(Å) | cell volume (Å³) | crystallinity (%) |
|---------|---------------------|---------------------|------------------|-------------------|
| Fresh   | 9.7793              | 9.3250              | 772.31           | 76.15             |
| Aged    | 9.7695              | 9.3225              | 770.56           | 76.16             |
| Used    | 9.7804              | 9.2952              | 770.02           | 79.22             |

Table 2 shows the cell constant of the sample calculated by the Debye-Scherrer formula. The crystallinity of Fresh, Aged and Used samples are 76.15%, 76.16% and 79.22% respectively. Compared with Fresh samples, Aged samples had no change, and the cell parameters and cell volume of Aged samples decreased. However, the crystallinity of Used samples increases obviously, the cell parameter alpha increases, while the cell volume decreases and the cell parameter beta decreases. It shows that Used samples has new crystalline phase formation, and the average lattice parameter of the whole sample decreases. The results of XRD analysis of CDPF show that the crystallinity of Used samples is higher than Fresh and Aged samples. On the one hand, the crystallinity of Used samples is increased because the precious metal oxides, metal oxides, residual soot and ash are divided into new crystalline phases in the aging process; On the other hand, the temperature of CDPF in the regeneration process may reach 800–900 °C, and in the aging process, the frequency of regeneration is relatively frequent, which is easy to cause the carrier grain growth, the crystal shape tends to be complete, increasing the crystallinity of the diesel vehicle durability aging sample, also shows that the CDPF deterioration degree of diesel vehicle durability test is stronger than that of laboratory hydrothermal aging.

Analysis of Surface Elements and Valence States by XPS

By means of XPS characterization of Fresh, Aged and Used samples, 0-1000 eV full scanning
spectra of the samples were carried out, and narrow scanning spectra of the atomic correlation orbits were carried out. The relative concentrations of Pt, Pd, Fe, Ce, Zr, O and S on the catalyst surface were calculated by integrating the peak areas of the atoms. As shown in Table 3, the concentrations of Pt, Pt$^{4+}$, different types of oxygen (surface oxygen OS, adsorbed oxygen Oad and lattice oxygen OL) and S are listed respectively.

Table 3. Surface atomic concentration of the CDPF sample (mole percent %).

| Samples | Pt  | Pt$^{4+}$ | O$_{1s}$ | O$_{S}$ | O$_{ad}$ | O$_{L}$ |
|---------|-----|-----------|----------|---------|---------|---------|
| Fresh   | 1.37| 0.70      | 96.8     | 29.7    | 31.0    | 36.1    | /       |
| Aged    | 0.80| 0.38      | 98.0     | 19.0    | 47.7    | 31.3    | /       |
| Used    | 0.43| 0.23      | 91.0     | 13.8    | 41.1    | 36.1    | 6.2     |

The concentrations of Pt atoms on the surface of Fresh, Aged and Used samples are 1.34%, 0.80% and 0.43%, respectively. The concentrations of Pt$^{4+}$ in high oxidation state also decreased by 0.70%, 0.38% and 0.23% respectively. Analysis of oxygen species concentration changes, the adsorption oxygen (Oad) concentration of Aged samples is the highest, 47.7%, followed by Used samples, adsorption oxygen concentration is 41.1%. Adsorption oxygen has a high mobility, is conducive to promoting the oxidative desorption of reactants in the active site. The lattice oxygen (OL) concentration on the surface of Aged samples is the lowest, 31.3%. The decrease of lattice oxygen concentration may mean the increase of oxygen vacancies. However, the lattice oxygen (OL) concentration on the surface of Aged samples and Fresh samples was 36.1%. The concentration of S of the Used samples is 6.2%.

Compared with Fresh samples, the concentrations of Pt atoms on the surface of Aged and Used samples were mostly decreased. The adsorbed oxygen concentration on the carrier surface of Aged and Used samples increased, while the lattice oxygen concentration decreased, indicating that different aging methods would increase the ratio of adsorbed oxygen and reduce the lattice oxygen ratio, thus affecting the adsorption, oxidation and desorption of reactants on the active sites of the carrier surface.

Catalytic Activity Evaluation

Fig.3 shows the ignition characteristic temperatures of Fresh, Aged and Used samples.

![Figure 3. The characteristic temperature of Fresh, Aged and Used samples.](image)

(“▲”Indicates that the conversion temperature of a sample to a gas exceeds 500 °C.)

The ignition temperatures of fresh, laboratory hydrothermal aging and diesel vehicle durability
agaging sample of CDPF are 118.4, 181.6 and 187.4 °C, respectively. The deterioration rates of CO ignition temperatures of Aged and Used samples are 53.4% and 58.3% respectively. The ignition temperatures of Fresh and Aged samples for C3H8 are 369.9 and 483.0 °C, respectively. The ignition temperature of diesel vehicle durability aging sample for C3H8 over 500 °C. The degradation rate of C3H8 ignition temperature of Used samples is higher than that of Aged samples. According to XPS surface element and valence analysis, the deterioration of CDPF activity is strongly correlated with the reduction rate of precious metal concentration on the surface of the carrier. On the other hand, the change of crystallinity of CDPF sample also has some effect on the degradation of catalytic activity. The crystallinity of Aged and Used samples increased greatly, which inhibits the migration of active oxygen and lattice oxygen and reduces the oxidation activity of the catalyst to a certain extent. The characteristic temperatures of Fresh and Used samples with 20% NO2 yield are 441.8 and 208.3 °C, respectively. The characteristic temperatures of 20% NO2 conversion rate of Aged samples is higher than 500 °C, while the temperature of 20% NO2 conversion rate of Used samples is decreased by 52.9%. The decrease of precious metal concentration on the surface of CDPF carrier after diesel vehicle durability aging means that the sintering and agglomeration of precious metals are obvious, and the size of Pt particles will grow up, which enhances the repulsion of Pt oxides, weakens the adsorption of oxygen and increases the oxidation capacity of NO. At the same time, the inhibition of NO oxidation to NO2 was weakened due to the decrease of adsorption and activity of CO and C3H8, which is one of the reasons for the enhancement of NO2 conversion activity. In conclusion, the Fresh samples have high activity and selectivity for CO and C3H8, while the Used samples have high activity and selectivity for NO2 yield, but poor activity for CO and C3H8. Compared with the Aged samples, the degradation rate of CO and C3H8 of Used samples is higher, but the activity of NO2 is higher.

Summary

The results of XRD analysis showed that the crystallinity of fresh, laboratory hydrothermal aging and diesel vehicle durability aging sample of CDPF are 76.15%, 76.16% and 79.22% respectively. The crystallinity of diesel vehicle durability aging sample was higher than that of fresh and laboratory hydrothermal aging sample.

By XPS characterization of the sample with different states of CDPF, the concentrations of Pt atoms on the surface of fresh, laboratory hydrothermal aging and diesel vehicle durability aging sample of CDPF are 1.34%, 0.80% and 0.43%, respectively. The concentrations of high oxidized Pt4+ also decreased, respectively, by 0.70%, 0.38% and 0.23%.

Through the evaluation of catalytic activity of samples in different states, the degradation of CO and C3H8 was deteriorated by laboratory hydrothermal aging and diesel vehicle durability aging samples of CDPF. The deterioration rate of CO and C3H8 ignition temperature of the diesel vehicle durability aging sample was higher than that of the laboratory hydrothermal aging sample. The results of XPS showed that the deterioration of CDPF activity was strongly related to the decrease of noble metal concentration on the surface of the carrier. In addition, the laboratory hydrothermal aging of CDPF and the crystallinity of the diesel vehicle durability aging sample increased greatly, which inhibited the reactive oxygen species and crystal lattice. The migration of oxygen reduced the oxidation activity of the catalyst to a certain extent.

The results of sample analysis and catalytic activity evaluation show that the deterioration degree of CDPF in 60,000 km vehicle aging test on diesel vehicle is stronger than that in laboratory simulation of high temperature hydrothermal aging.

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