Application News

No. P112

EPMA-8050G Electron Probe Microanalyzer

Analysis of Automotive Three-Way Catalyst

In modern society, environmental countermeasures have evolved with the progress of motorization together with high economic growth. Automotive exhaust gas purification catalysts purify the toxic substances in exhaust gas to substances which are harmless to the human body. Responding to the increasingly stringent standards applied to exhaust gas in recent years, active research and development are being carried out in order to satisfy high requirements for purification performance, heat resistance, low temperature activity, and high temperature durability.

The three-way catalyst (TWC) is an automotive catalyst system that was applied practically in the 1970s, and uses a combination of three elements to detoxify the harmful components in exhaust gas. Platinum (Pt) and palladium (Pd) oxidize HC (hydrocarbons) to H_2O (water) and CO_2 (carbon dioxide) and oxidize CO (carbon monoxide) to CO_2, while Rh (rhodium) reduces NO_x (nitrogen oxides) to N_2 (nitrogen).

This article introduces an example of analysis of a three-way catalyst using an EPMA-8050G EPMA™ electron probe microanalyzer.

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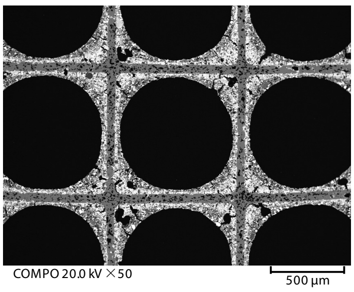

Fig. 1 COMPO Image of Rh-Pd System Three-Way Catalyst

Structure of Three-Way Catalysts

Three-way catalysts comprise precious metal catalysts such as Rh, Pd, and Pt, an alumina (Al_2O_3) carrier which disperses the particles of precious metals, and a precious metal carrier layer (washcoat layer) consisting of base metal oxide catalytic promoter components which promote a catalytic reaction, on a monolithic substrate with a ceramic ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$ cordierite) or metal honeycomb structure. The COMPO image in Fig. 1 shows a ceramic honeycomb structure.

Because automotive catalysts must maintain a certain level of purification performance through the use period of the automobile, severe durability tests are conducted focusing on heat deterioration and catalyst poisoning deterioration. Where heat deterioration is concerned, since it is necessary to suppress grain growth of precious metals of trace amounts of Rh, Pd, and Pt at high temperatures, the focus is on the dispersion condition of the precious metals and the carrier metal before and after the durability test. In catalyst poisoning deterioration, the performance of the catalysts deteriorates due to a reduction of the specific area of the Al_2O_3 carrier or covering of the precious metal surface by components such as P, S, Ca, Mn, Zn, and Pb, which are contained in gasoline and oil. Therefore, the focus of the poisoning durability test is the differences in the condition of permeation at the inlet, interior, and outlet of the catalyst.

Fig. 2 shows the results of mapping analysis of a Rh-Pd system three-way catalyst. It can be understood that trace amounts of the precious metals Rh and Pd are distributed on the upper layer of a two-layer washcoat layer, and promoters such as CeO_2, ZrO_2, La_2O_3, Nd_2O_3, and BaO are composed of different composition ratios in the two (upper and lower) layers.

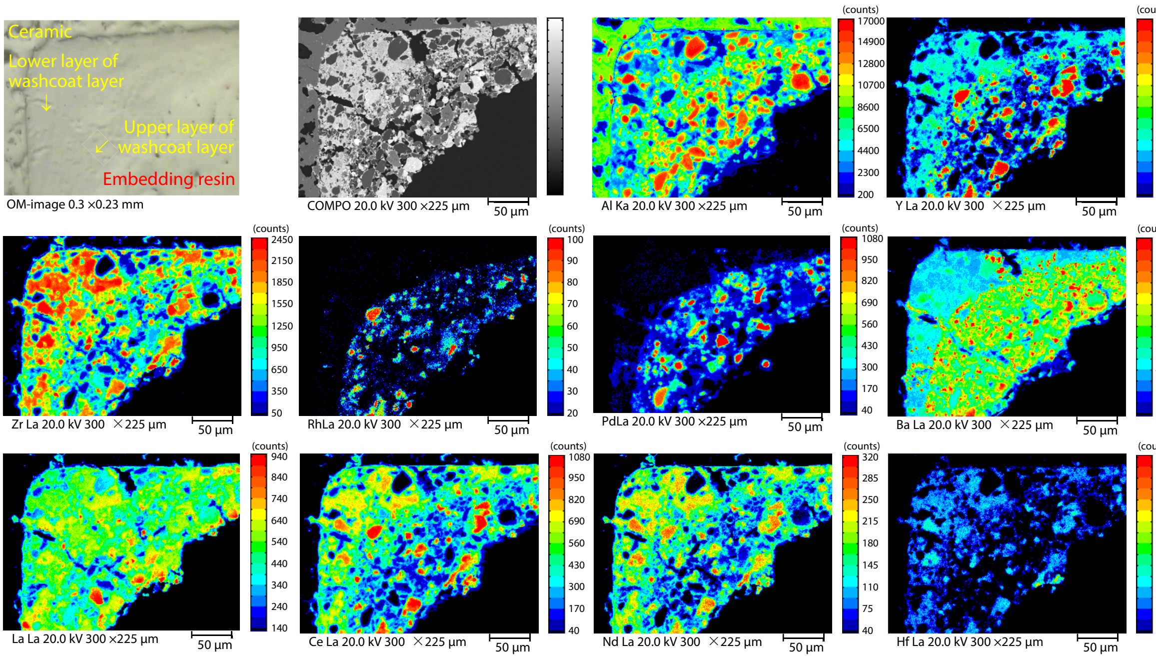

Fig. 2 Mapping Analysis of Rh-Pd System Three-Way Catalyst

Promoters and Carrier of Three-Way Catalyst

The promoter CeO_2 has an oxygen storage capacity. La_2O_3 promotes NO_x purification activity in the low temperature region, while BaO improves durability and Y_2O_3 and Nd_2O_3 stabilize ZrO_2. The CeO_2-ZrO_2 system complex oxide promoters to which these compounds are added suppress the grain growth of the precious metals by maintaining the specific area of CeO_2 under a high temperature atmosphere. In Al_2O_3, which is the carrier, it is necessary to maintain a high dispersion state of the precious metal components on the carrier and keep the specific area at high temperatures in order to display high purification activity.

Fig. 3 shows the results of an enlarged mapping analysis of the upper layer in Fig. 2. La affects the structure of the Al_2O_3 carrier, resulting in improved heat resistance. In addition, the precious metals Rh and Pd are distributed in the Al_2O_3 carrier, and the presence of compounds of Rh and Pd can be confirmed in some particles.

Phase Analysis

In Fig. 4, point sets (clusters) are extracted in the binary scatter plots of Rh-Pd, Al-Pd, Rh-La, and Pd-La, and the compound phases are shown. From the phase diagram, it can be understood that Rh and Pd are deposited on the Al_2O_3 carrier and complex oxides in multiple patterns. The 3D scatter plots (XYZ) in Fig. 5 assign six elements (Al, Zr, Rh, Pd, La, Ce) to the + and – directions of the X, Y, and Z axes. The stereo 3D scatter plots are presented stereoscopically, making it possible to capture the clusters of compound phases virtually.

Conclusion

Catalyst performance can be improved by investigating the locations where trace amounts of precious metals are deposited on the Al_2O_3 carrier and complex oxide particles, and improving the carrier and promoters.

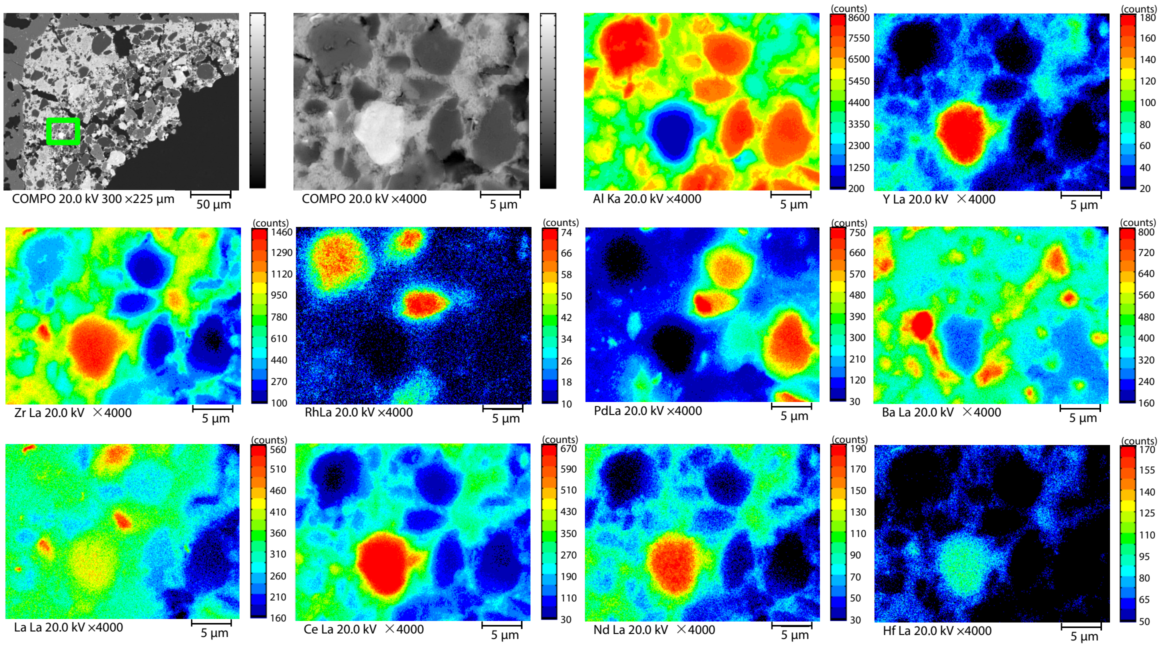

Fig. 3 Mapping Analysis of Upper Layer of Rh-Pd System Three-Way Catalyst

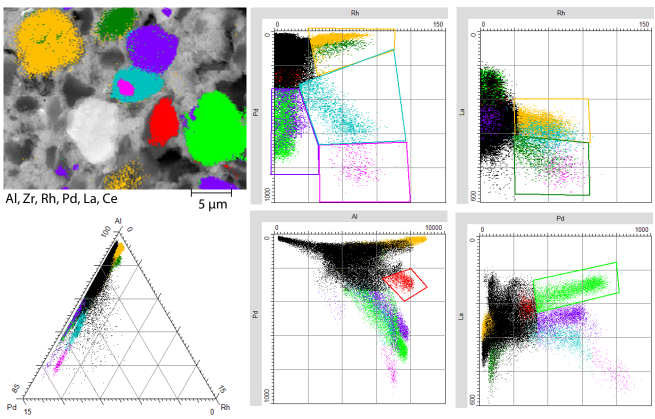

Fig. 4 Phase Diagram and Scatter Plots

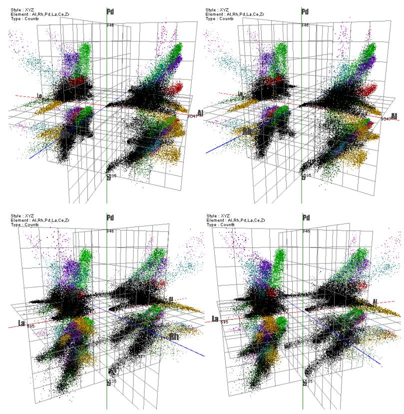

Fig. 5 Stereo 3D Scatter Plots (XYZ)

<Reference>
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