Emission-Control Catalysts

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Self-Regenerating Rh- and Pt-Based Perovskite Catalysts for Automotive-Emissions Control**

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Automotive catalysts deteriorate as a result of a decrease in the active surface area of the precious metals, this is caused by the growth of grains under the inherent redox environment of exhaust gases at high temperatures of up to 1000 °C. To compensate for this deterioration, conventional catalysts are loaded with an excess amount of precious metals, although this leads to over-consumption and supply problems. Self-regenerating catalysts, which suppress the grain growth of precious metals, have recently been successfully developed and are based on the repeated movement of the precious metals in and out of perovskite oxides between a solid solution and metallic nanoparticles during the natural changes in the redox conditions.[1] Herein, we report for the first time that this self-regenerating function is realizable in Pt and Rh, as well as in Pd.

It has been predicted that the demand for precious metals for automotive catalysts will increase, and that these metals will soon be in short supply as a result of the growth in the number of automobiles in China and India and the global

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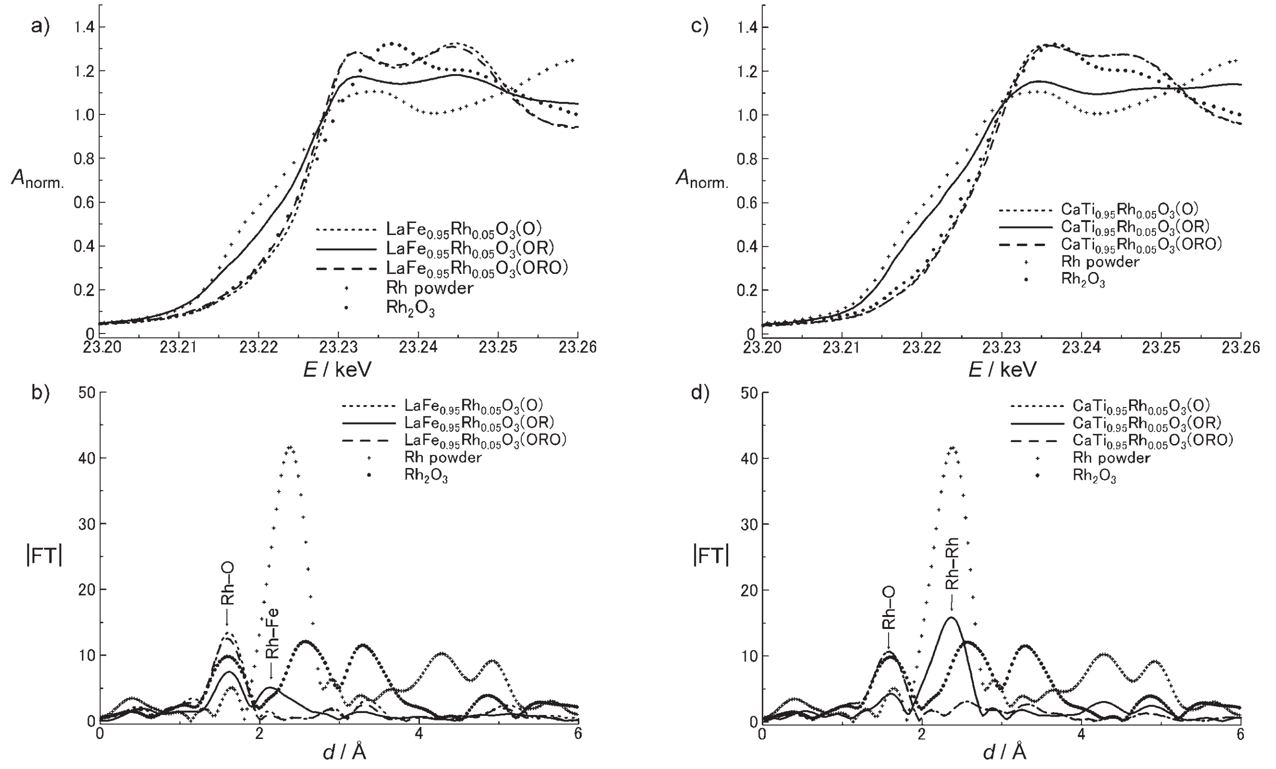
strengthening of emission controls. Three precious metals, namely Pd, Rh, and Pt, are used in catalytic converters for gasoline automobiles. Of these, Pt is expected to be in particularly short supply as it is also used as a catalyst for diesel engines and will soon be in demand as an electrode catalyst for fuel cells. The amount of Rh available from mining is limited, and the supply of Rh has been especially unstable in recent years. In automotive catalysts, Pd shows the biggest deterioration among these precious metals because it has the lowest melting point. To solve this problem, a technology based on the self-regenerating function of Pd-perovskite was introduced.[1,2] The possibility of applying this catalyst technology to Pt and Rh as well would solve the issue of supply and demand for precious metals and have a marked socio-economic effect.

The structure of perovskite, which has the generalized formula ABO_3, where A is the larger cation and B is the smaller cation, is adaptable and gives rise to materials that have a wide array of properties.[3] Many combinations of elements form perovskites, and these can be partially substituted when the tolerance factors are met. To maintain electroneutrality, three combinations are possible: $A^{1+}B^{5+}O_3$, $A^{2+}B^{4+}O_3$, and $A^{3+}B^{3+}O_3$. $BaTiO_3$ (an $A^{2+}B^{4+}O_3$ combination) is an electroceramic that is used in capacitors and transducers but not as a catalyst. $LaCoO_3$ is an $A^{3+}B^{3+}O_3$ perovskite whose catalytic properties have attracted attention since the 1970s,[4] and $LaFe_{0.95}Pd_{0.05}O_3$ has been used industrially as a three-way catalyst for gasoline automotive-emission control since October 2002.

To study the self-regenerating properties, perovskite catalysts containing Pd, Rh, or Pt were prepared by the alkoxide method.[1] X-ray absorption fine structure (XAFS) measurements were carried out on samples that were oxidized (O), reduced (OR), and re-oxidized (ORO). The X-ray absorption near-edge structure (XANES) spectrum at the Rh K-edge (23.220 keV) for $LaFe_{0.95}Rh_{0.05}O_3$ after each treatment is shown in Figure 1 a, and the calculated radial structure function around Rh is shown in Figure 1 b. The local



Sample	Shell	CN	IAD (Å)	D-WF (Å^2)	R-factor (%)
O	Rh-O	6*	2.041(6)	0.0025(7)	1.4
OR	Rh-O Rh-Fe	3.1(3) 1.2(3)	2.046(9) 2.575(9)	0.0025* 0.0033(15)	5.0
ORO	Rh-O	5.8(3)	2.038(5)	0.0025*	1.4

Sample	Shell	CN	IAD (Å)	D-WF (Å^2)	R-factor (%)
O	Rh-O	6*	2.028(6)	0.0052(7)	1.2
OR	Rh-O Rh-Rh	1.8(1) 5.1(2)	2.022(6) 2.676(2)	0.0052* 0.0062(2)	0.3
ORO	Rh-O	6.0(1)	2.030(3)	0.0052*	0.3

*: Fixed parameter, CN: coordination number, IAD: interatomic distance, D-WF: Debye-Waller factor.

Figure 1. Comparison of the X-ray absorption data for $LaFe_{0.95}Rh_{0.05}O_3$ and $CaTi_{0.95}Rh_{0.05}O_3$, together with Rh_2O_3 and Rh powder as reference materials. XANES spectra were measured near the Rh K-edge for $LaFe_{0.95}Rh_{0.05}O_3$ (a) and $CaTi_{0.95}Rh_{0.05}O_3$ (c). The valence state of Rh changes reversibly in a redox cycle. The radial structure function around Rh was calculated as the magnitude of the Fourier transform (FT) of the k^3-weighted EXAFS oscillations for $LaFe_{0.95}Rh_{0.05}O_3$ (b) and $CaTi_{0.95}Rh_{0.05}O_3$ (d). The results of parameter fitting are shown in the tables. The parameters marked with * were fixed. The coordination number (CN) for Rh–O bonding should be six in the perovskite structure, and the decrease of this number after reduction indicates the separation of Rh from the structure.

structure parameter estimated by extended X-ray absorption fine structure (EXAFS) analysis is given in the tables in Figure 1.[5] All the Rh in $LaFe_{0.95}Rh_{0.05}O_3$ is present as a solid solution in perovskite after oxidation, and only 37% of the Rh becomes isolated as metallic nanoparticles even after reduction at 800 °C. Moreover, it becomes clear that Rh forms an alloy with Fe. Replacement of the perovskite with $CaTiO_3$ decreases the Rh–O bonding and increases the Rh–Rh bonding after reduction (Figure 1 d). In this case about 73% of the Rh is separated from the perovskite to form metallic Rh nanoparticles. The XANES spectrum at the Rh K-edge for reduced $CaTi_{0.95}Rh_{0.05}O_3$ shifts towards the energy for metallic Rh powder, thus implying that a greater proportion of Rh is in the metallic state (Figure 1 c). The edge positions of Rh for oxidized and re-oxidized $CaTi_{0.95}Rh_{0.05}O_3$ are slightly higher than that of the trivalent Rh seen in Rh_2O_3.

To determine whether Rh and Pt form a solid solution with the perovskite structure or not an X-ray anomalous diffraction (XAD) study was carried out. Figure 2 shows the powder X-ray diffraction (XRD) pattern in the limited range of momentum transfer Q for $CaTi_{0.95}Rh_{0.05}O_3$ and $CaTi_{0.95}Pt_{0.05}O_3$ after oxidation. Two Bragg reflections from the sample can be assigned to the pseudocubic cell of the perovskite structure. The structure factor for the (100) reflection can be expressed approximately in the form: $F(100) \propto ||f_A - f_B - f_O|$, where f_A, f_B, and f_O are the atomic scattering factors for the A-site, B-site, and oxygen atoms, respectively. The insets in Figure 2 represent the energy dependence of the (100) reflection intensity near the Rh K-edge and the Pt L_{III}-edge (11.562 keV), respectively. The dip of the X-ray intensity near the edge energy clearly indicates that both Rh and Pt occupy the B-site of the $CaTiO_3$-type perovskite structure since $|f_{Ca}|$ is always less than $|f_{Ti}|$ in this energy range.

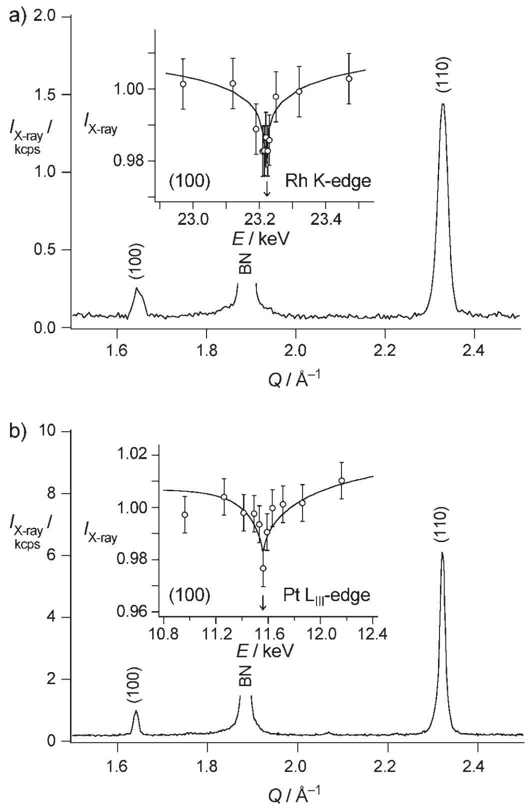


Figure 2. X-ray powder diffraction patterns of $CaTi_{0.95}Rh_{0.05}O_3$ (a) and $CaTi_{0.95}Pt_{0.05}O_3$ (b) around the Bragg reflections (100) and (110) for the pseudocubic cell of the perovskite structure. The oxidized samples contain BN as a binder. The insets give the energy dependence of the (100) reflection intensity near the absorption edges for Rh and Pt, respectively.

The proportion of precious metal present in the perovskite lattice as a solid solution was calculated from the coordination number of the first nearest neighbor with oxygen (Pd–O, Rh–O, or Pt–O bonds) and is given in Figure 3 for various combinations of precious metals with perovskite-type oxides. Under oxidizing conditions, $LaFe_{0.95}Pd_{0.05}O_3$, $CaTi_{0.95}Rh_{0.05}O_3$, $SrTi_{0.95}Rh_{0.05}O_3$, $BaTi_{0.95}Rh_{0.05}O_3$, $CaTi_{0.95}Pt_{0.05}O_3$, and $CaZr_{0.95}Pt_{0.05}O_3$ form perfect solid solutions and show a large difference in the proportion of precious metal present in the perovskite lattice during the redox alternations. This difference is defined the self-regeneration ratio. The $A^{2+}B^{4+}O_3$ perovskites, with $CaTiO_3$, a natural mineral, as a component, have not been considered to have catalytic activity. However, we show in this study that various oxides, including an $A^{2+}B^{4+}O_3$ combination, can be used as catalyst materials, as can an $A^{3+}B^{3+}O_3$ perovskite.

The effect on the suppression of growth of Pt grains in an actual engine exhaust gas was investigated. $CaTi_{0.98}Pt_{0.02}O_3$ and Pd/γ-Al_2O_3 catalysts were exposed to engine exhaust gas at 900 °C for 100 h. The Pt grains were then observed by TEM (Figure 4). The Pt grains on alumina grew to over 100 nm, whereas only fine metallic grains about 1–3 nm in diameter were found on the perovskite surface.

We have therefore demonstrated that a precious-metal-containing perovskite catalyst can function as an "intelligent" catalyst that regenerates itself to maintain a high activity in a cycle that involves a solid solution and segregation even in a harsh redox environment at high temperatures.[1] The following considerations are important when designing an intelligent catalyst: the oxide, which makes the perovskite component, should maintain a stable structure so that it can capture and release the precious metal at high temperatures under a redox environment. Under reducing conditions, the precious metal emerges from the oxide to form metallic clusters or nanoparticles that demonstrate a higher catalytic activity. At the same time, the perovskite oxide releases oxygen and retains its electroneutrality. This release of oxygen is detectable by a weight change.[6] Under oxidizing conditions, the precious metal and oxygen are reabsorbed into the perovskite oxide. The precious metal repeats the cycle of forming a solid solution and segregation as a result of the inherent cycling between an oxidizing and a reducing environment.

In conclusion, the precious metals Pd, Rh, and Pt can all be used in new self-regenerating catalysts that suppress the grain growth. Although perovskite-type oxides are very useful because of their structural stability and their abundance of combinations, the possibility of using other oxides with different crystal structures cannot be neglected. Moreover, a self-regenerating Pd-perovskite catalyst has been reported by

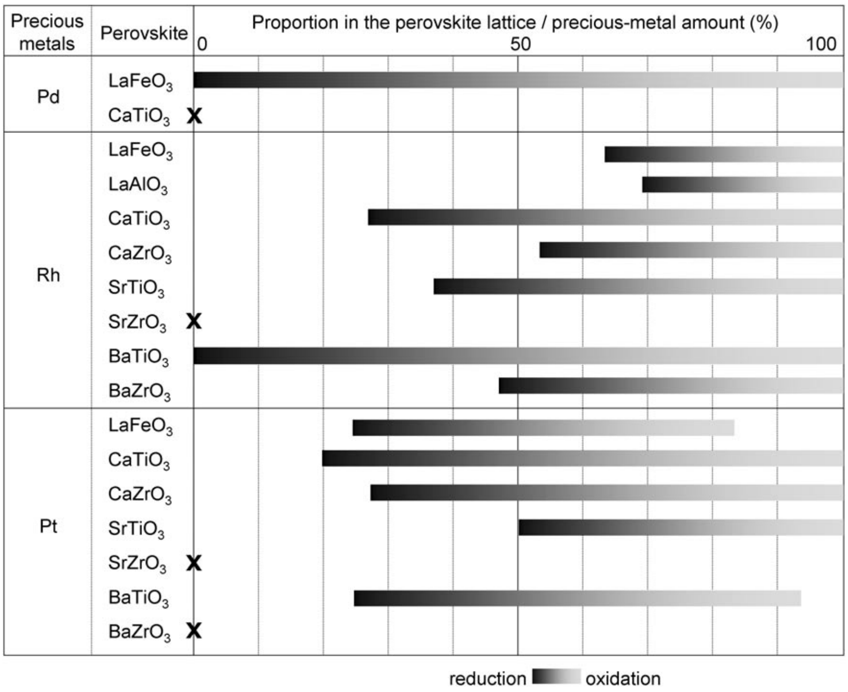


Figure 3. Comparison of the solid solution of the precious metal for various perovskites. A longer bar indicates a better self-regeneration performance. **X** indicates that the precious metal does not form a solid solution with the perovskite.

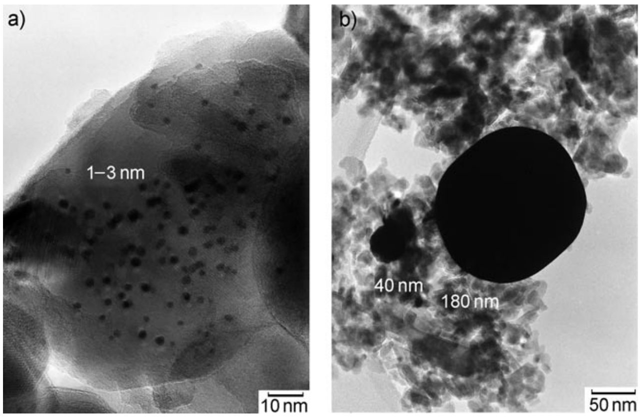


Figure 4. TEM images of Pt grains of catalysts aged in engine exhaust at 900 °C for 100 h. $CaTi_{0.95}Pt_{0.05}O_3$ (a) was observed at a magnification of 400 000 and Pt/γ-Al_2O_3 (b) at a magnification of 100 000.

the group of Ley and Smith to show a high activity and a long life in organic synthesis reactions, such as the Suzuki coupling.[7] The application of this technology could be extended to diesel after-treatment and to pharmaceutical synthesis, and this technology may solve the socio-economic issues relating to the supply and demand of precious metals.

Experimental Section

Preparation of powder catalysts: All the precious-metal-containing perovskite catalysts were prepared by the alkoxide method.[1] Metal ethoxyethylates $[M(OC_2H_4OC_2H_5)_3]$ ($M = La^{3+}$, Fe^{3+}, or Al^{3+}) or metal isopropoxides $[M^{x+}\{OCH(CH_3)_2\}_x]$ ($M = Ca^{2+}$, Sr^{2+}, Ba^{2+}, Ti^{4+}, or Zr^{4+})} were dissolved in toluene. The precious-metal acetylacetonate $[M^{x+}(CH_3COCHCOCH_3)_x]$ ($M = Pd^{2+}$, Rh^{3+}, or Pt^{2+}) was also dissolved in toluene. The amount of each precious metal was adjusted to 5 atom % of that of the B-site element of the perovskite structure. Precipitates containing the precious metal were obtained upon hydrolysis with deionized water. The precursor was dried and then calcined at 800 °C for 2 h in air to obtain a perovskite powder catalyst containing homogeneously distributed precious metal. To prepare the conventional catalysts, powdered γ-Al_2O_3 ($SSA = 120\ m^2 g^{-1}$) was impregnated with dilute aqueous $Pd(NO_3)_2$, $Rh(NO_3)_3$, or $(NH_3)_2Pt(NO_2)_2$, dried, and calcined at 500 °C for 1 h in air.

XAFS and XAD analyses: The thermal treatment of the catalyst for X-ray measurements was carried out in three steps.[1] The powdered catalyst was sequentially oxidized (O) in air at 800 °C for 1 h, reduced (OR) in 2.5 % H_2 and 7.5 % CO balanced with N_2 at 800 °C for 1 h, and then re-oxidized (ORO) in air at 800 °C for 1 h. After each step the sample was cooled to room temperature under the same atmosphere to make sure that its state did not change, and then pressed into pellets. XAFS measurements were carried out in transmission mode at the BL01B1 beamline of the SPring-8 8 GeV synchrotron radiation source in Japan. EXAFS oscillations were analyzed with the standard procedure, using the FEFF code.[1] XAD measurements on $CaTi_{0.95}Rh_{0.05}O_3$ and $CaTi_{0.95}Pt_{0.05}O_3$ oxidized at 800 °C were carried out at the same beamline to determine the distribution of Rh and Pt in the perovskite crystal structure.

Rapid ageing of monolithic catalysts: $CaTi_{0.98}Pt_{0.02}O_3$ and Pt/γ-Al_2O_3 catalysts were coated on the inner wall of a monolithic honeycomb substrate (80 mm in diameter and 95 mm in length with a grid of 64 cells cm^{-2}) containing the same amounts of Pt (3.37 mg cm^{-3}).[1] The two monolithic catalysts were attached to each side-bank in the exhaust system of an automotive 4-L V8 engine for simultaneous ageing treatment. The monolithic catalysts were then exposed to high-temperature exhaust gas at 900 °C for 100 h by alternating a large redox fluctuating atmosphere ($\Delta\lambda = \pm 4\%$ at 0.6 Hz) around the stoichiometric point for 870 s and an oxidating atmosphere for 30 s. This ageing procedure is widely accepted as simulating a driving strategy that achieves high fuel economy by introducing fuel cut-off during deceleration.

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