SELF-REGENERATION OF A Pd-PEROVSKITE CATALYST: A PHILOSOPHER'S STONE FOR TODAY'S AUTOMOTIVE ENGINE

The important role of automotive catalysts is widely recognized for the conversion of three pollutant-emissions, such as carbon monoxide (CO), nitrogen oxides (NOx) and unburned hydrocarbons (HC) in engine exhaust gases. The conventional catalysts disperse fine particles of precious metal on ceramic-support materials. However, the catalytic activity deteriorates owing to the agglomeration and growth of metal particles during vehicle use (see the lower sequence in Fig. 1). Thus, an excess amount of precious metals is usually incorporated to guarantee continued catalytic activity after running the vehicle over 80,000 km. A state-of-the-art automotive gasoline engine is operated close to the stoichiometric air-to-fuel ratio to convert the pollutant-emissions simultaneously [1], accompanying with redox (reduction and oxidation) fluctuations in exhaust-gas composition by adjusting the air-to-fuel ratio. A perovskite-based catalyst, $LaFe_{0.57}Co_{0.38}Pd_{0.05}O_3$, has maintained its high activity with high dispersion of precious metals. In this study, we have found self-regeneration of the perovskite-based catalyst with environmental fluctuations, using X-ray diffraction and XAFS performed at beamline **BL14B1** [2].

The palladium-containing perovskite (Pd-perovskite) catalyst was prepared by the alkoxide method [3,4]. The thermal ageing procedure was carried out in three steps to simulate the redox fluctuations of an automotive exhaust gas: at first the powdered catalyst was oxidized in the air at 800 °C for 1 hour, then reduced in an atmosphere of 10% H_2/ 90% N_2 at 800 °C for 1 hour, and finally re-oxidized in the air at 800 °C for 1 hour. Figure 2(a) depicts the powder diffraction pattern for the three samples. Two Bragg reflections (100) and (110) were observed for the oxidized catalyst. The Bragg reflections shifted and a few additional peaks appeared for the reduced catalyst, indicating lattice expansion and partial demolition of the perovskite crystal in a reductive atmosphere. Surprisingly, the

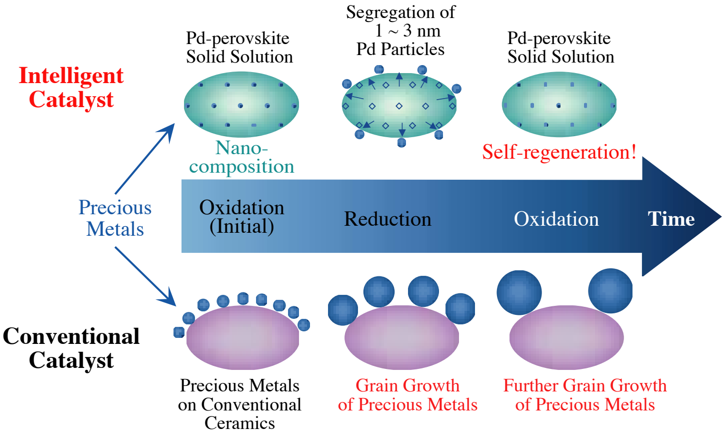

Fig. 1. Self-regeneration of the intelligent catalyst (upper sequence) and deterioration of the conventional catalyst (lower sequence) in the exhaust-gas of the state-of-the-art gasoline engine.

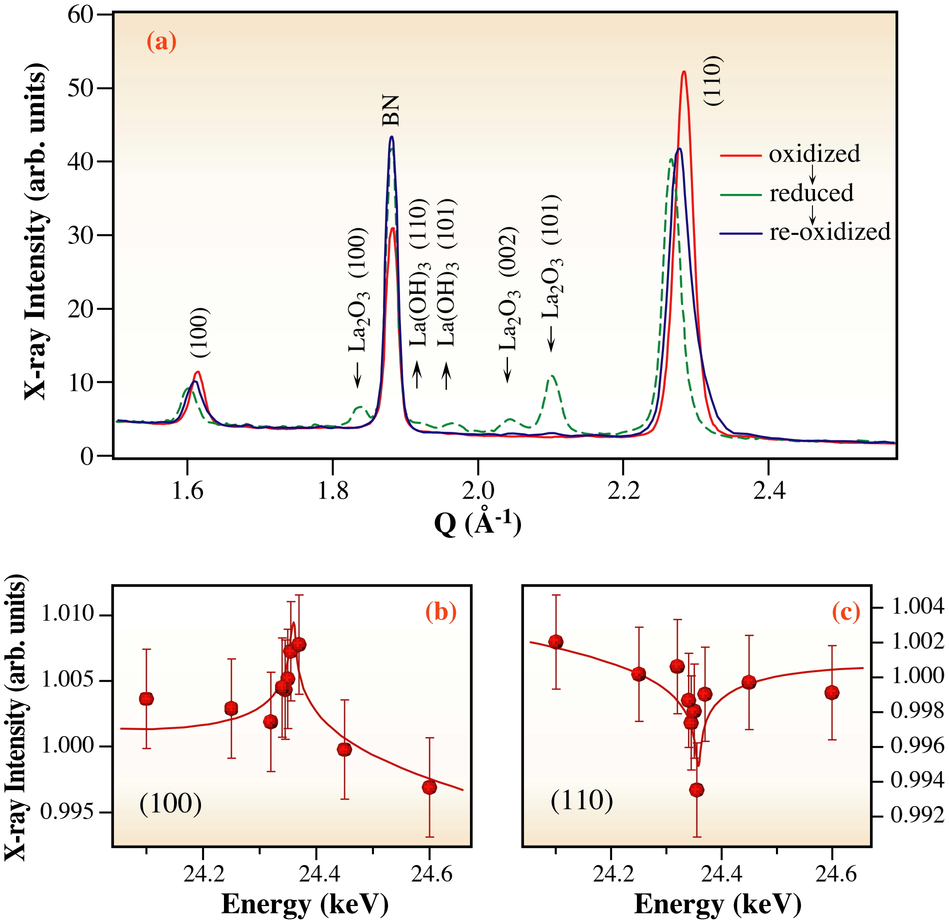

Fig. 2. X-ray powder diffraction. ***(a)*** *Powder X-ray diffraction pattern for three aged catalysts,* $LaFe_{0.57}Co_{0.38}Pd_{0.05}O_3$*, which were pressed into pellets with a BN binder after the ageing. Two Bragg peaks from the catalysts were assigned as a pseudocubic cell of the perovskite structure. The perovskite crystal in a reductive atmosphere was partially destroyed and transformed into* $La(OH)_3$ *through* La_2O_3*. Energy dependence of the intensity for* ***(b)*** *(100) and* ***(c)*** *(110) reflections near the Pd K-edge indicates that the B-site of the perovskite structure is occupied with Pd in the oxidized catalyst.*

diffraction pattern recovered at the re-oxidizing step: the Bragg reflections shifted back and the additional peaks disappeared completely. The catalyst retains a predominantly perovskite structure throughout the redox cycle. The increase of (100) and the decrease of (110) reflection intensities at the Pd *K*-edge clearly show that Pd occupies the B-site (6-fold coordination) of the perovskite lattice in the oxidative atmosphere (Figs. 2(b) and 2(c)).

Figure 3(a) shows XANES spectra for Pd-perovskite catalysts after the each ageing step to estimate the valence state of Pd. The chemical shift of the edge position implies that the valence of Pd in the oxidized or re-oxidized catalyst is higher than the normal bivalence as seen in PdO. On the other hand, Pd is in the metallic state in the reduced catalyst. The local structure around Pd also reversibly changes, depending on the redox atmospheres (Fig. 3(b)). The first peak of the radial structure function can be fitted as 6 oxygen atoms of a PdO_6 octahedron for the oxidized and re-oxidized catalysts, while it can be fitted as Pd and Co atoms in a Pd-Co alloy particle for the reduced catalyst.

It has been proved that the particle growth of the precious metal can be suppressed as a result of this Pd movement between inside and outside the perovskite lattice due to the structural responses to the redox fluctuations in exhaust-gas composition with the state-of-the-art gasoline engine (see the upper sequence in Fig. 1). Therefore, this catalyst can refresh by itself to maintain the activity while the vehicle is being driven, and can reduce by 70 - 90% the amount of precious metals needed to meet the ultra-low emission vehicle standards.

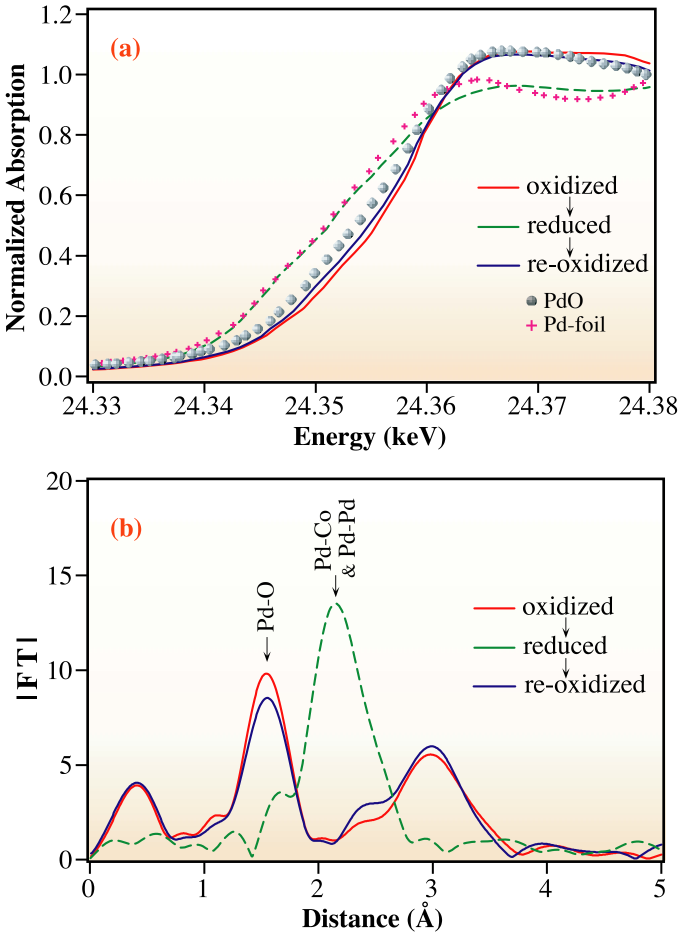

*Fig. 3. Comparison of XAFS. **(a)** X-ray absorption spectra near the Pd K-edge, which were measured in transmission mode, for three aged catalysts, $LaFe_{0.57}Co_{0.38}Pd_{0.05}O_3$. Those for PdO and a Pd-foil are also shown as reference materials. The valence of Pd changes reversibly in a redox cycle. **(b)** Radial structure function around Pd: Magnitude of Fourier transform (FT) of the k^3-weighted EXAFS oscillations for the catalysts. Neighbours seemingly appear closer to the X-ray absorbing atom because the phase shift of the photoelectron was not taken into account. The local structure around the Pd atom changes reversibly, too.*

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