Structural Investigation of Model Planar Perovskite-Supported Precious-Metal Catalysts

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Introduction

The Daihatsu Intelligent Catalyst [1] is based on an ingenious cyclical process for promoting high precious-metal dispersion as a result of exposure to three-way automotive exhaust-gas catalyst operating conditions: perovskite-supported precious-metal particles alternately disperse as cations into the perovskite lattice under leans conditions and then reform as small metallic particles under rich conditions [2]. As yet, the mechanism by which these structural transformations occur apparently has not been elucidated, and the actual morphology of the catalyst, including the precious-metal dispersion, has not been examined in detail. We have thus undertaken a fundamental study of the Intelligent Catalyst using idealized model planar catalyst geometry in combination with analytical and high-resolution transmission electron microscopy.

Materials and Methods

$CaTiO_3$ and $LaFeO_3$ model catalyst supports (single crystal films with thicknesses in the range of 30-100 nm) were grown by pulsed laser deposition (PLD) on (001) $SrTiO_3$ substrates, and thin (of order 1 nm thick) layers of Pt, Rh, or Pd were vacuum-deposited onto the perovskite film surfaces. The resulting model catalysts were then subjected to varying cycles of oxidation (1 hr, 800° C, dry air) and reduction (1 hr, 600° C, 1% H_2 in N_2) in order to induce structural changes. TEM specimens were finally prepared from the model catalysts by standard methods and examined by a combination of high resolution TEM (HRTEM), scanning TEM (STEM), selected-area electron diffraction (SAED), x-ray energy-dispersive spectroscopy (XEDS), and electron energy-loss spectroscopy (EELS).

Results and Discussion

Preliminary results are consistent with the basic process described above. For example, upon oxidation, TEM images show no Pt on the surface of the $CaTiO_3$ film. However, numerous structural defects, distinct from the surrounding perovskite matrix, form, as shown in Fig. 1(a). Upon reduction, these defects mostly disappear, and metallic Pt particles are found on the surface of the film, as shown in Fig. 1(b). This sequence of events was observed upon a second, subsequent, red-ox cycle and was also found to occur in the Pd-on-$LaFeO_3$ system.

Significance

This work should ultimately provide fundamental insight into the nature of the phenomena underlying the Daihatsu Intelligent Catalyst concept. Such information will hopefully spur further development and greater implementation of this potentially promising new technology.

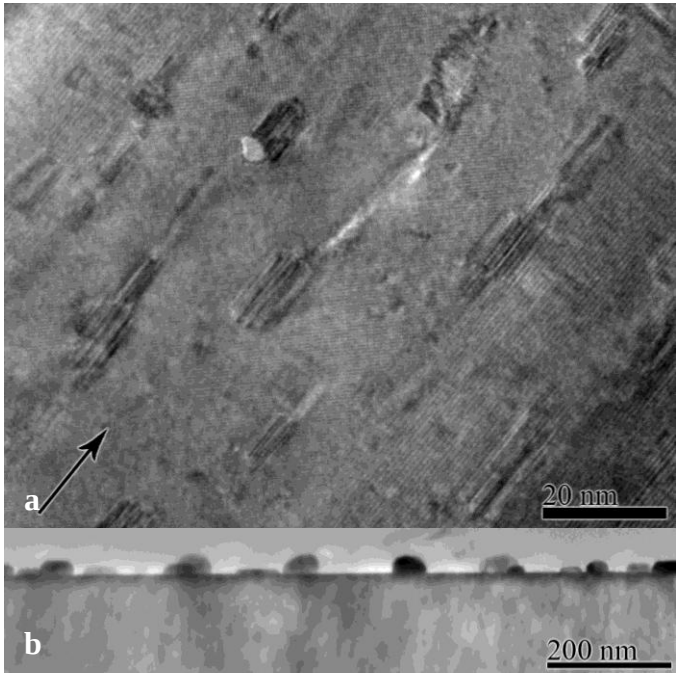

Figure 1.(a) Defects formed within the $CaTiO_3$ film of the Pt-on-$CaTiO_3$ sample upon oxidation and (b) the Pt particles forming on the surface of the same sample upon reduction. The arrow in (a) points toward the film surface.

References

1. Nishihata, Y., Mizuki, J., Akao, T., Tanaka H., Uenishi, M., Kimura, M., Okamoto, K., Hamada,N., *Nature* 418 (2002) 164.
2. Tanaka, H., Uenishi, M., Taniguchi, M., Tan, I., Narita, K., Kimura, M., Kaneko, K., Nishihata, Y., Mizuki, J., *Catal. Today* 117 (2006) 321.