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Reversible precipitation/dissolution of precious-metal clusters in perovskite-based catalyst materials: Bulk versus surface re-dispersion

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ABSTRACT

High-angle annular dark-field imaging with aberration-corrected scanning transmission electron microscopy unambiguously establishes that nanometer-size Pt-rich clusters reversibly precipitate and dissolve under reducing and oxidizing conditions, respectively, within the oxide matrix of Pt-doped $CaTiO_3$, previously proposed as a novel self-regenerating perovskite-based three-way catalyst. In fact, most of the Pt-rich clusters formed upon reduction are within the oxide matrix and thus unavailable for gas-phase catalysis. Those clusters of Pt that do form on the surface tend to coarsen rather than dissolve upon oxidation.

1. Introduction

Cyclical re-dispersion of the precious metals in novel perovskite-based three-way catalysts (TWCs) for automotive emissions control has been proposed as a means of dramatically improving catalyst durability, thereby allowing for more efficient precious metal utilization [1,2]. The idea is based largely on X-ray absorption measurements (X-ray absorption near-edge structure and extended X-ray absorption fine structure, XANES and EXAFS, respectively), from which it was concluded that nanoparticles of precious metal can dissolve into and reform out of a particular perovskite under high temperature oxidizing and reducing conditions, respectively. Since such fluctuations in exhaust gas composition are normally imposed at a frequency of about 1 Hz by the TWC engine-control system, the repeated re-formation of nanoparticles in situ would naturally result in self-regeneration of the catalyst [3], according to the idea's proponents.

Historically, perovskite-based precious-metal catalysts have been of interest since the 1970s [4], and a number of recent studies that cite the work on self-regeneration above may be found in the literature [5,6]. Typically, the focus is on either perovskite-supported metal catalysis, where strong interactions between metal and support are apparent [5], or metal-doped perovskite catalysis, where intrinsic activity may be unusual [6]. Little attention, however, has been given to establishing the extent to which cyclical re-dispersion, intended to maintain high dispersion of supported metal particles, actually occurs in these catalysts.

We thus recently initiated investigations of the atomic-scale processes underlying the self-regenerating catalyst concept using spherical-aberration (C_s)-corrected scanning transmission electron microscopy (STEM) to examine both powder catalysts and cross-sectional specimens of model planar catalysts. In our initial studies [7], focused on the Pd-$LaFeO_3$ system, we were surprised to observe that both elementary processes, Pd particle formation on the surface of the Pd-doped perovskite, $LaFe_{0.95}Pd_{0.05}O_{3-\delta}$, as well as Pd particle dissolution into $LaFeO_3$, are much more limited than we expected, based on the original reports. For example, only a minute fraction of the Pd, i.e., that located within just a few nanometers of a free surface of the doped perovskite, appeared on the surface upon reduction (10% H_2/N_2 at 800 °C for 1 h). It is important to realize, however, that the original work sampled the bulk [1–3], while our observations of Pd nanoparticle formation, as in this example, were limited to the surface, due to the low contrast of Pd against $LaFe_{0.95}Pd_{0.05}O_{3-\delta}$.

In the present study, we consider some of the other proposed systems [2], exemplified by Pt-$CaTiO_3$, that are more amenable to high-angle annular dark-field (HAADF) imaging in STEM mode because of the higher contrast provided by the relatively heavier

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precious-metal atoms against their lighter perovskite-support atoms. Our main finding is that nanometer-size Pt-rich clusters readily form upon reduction and tend to re-dissolve upon oxidation, but that most of them remain well within the perovskite, where they are essentially inaccessible for gas-phase catalytic reactions.

2. Experimental details

The citrate method was used to synthesize $CaTi_{0.95}Pt_{0.05}O_{3-\delta}$ powder. Stoichiometric amounts of $Ca(NO_3)_2 \cdot 4H_2O$, $Ti[O(CH_2)_3CH_3]_4$, and $PtC_{10}H_{14}O_4$ (Alfa Aesar) were dissolved in de-ionized water with citric acid, and nitric acid was used to control the solution pH. The solution was dehydrated at 100 °C and held at 60 °C until it formed a gel, which was then calcined at 800 °C in flowing oxygen. A portion of the resulting powder was then pressed and sintered at 1200–1300 °C to form a dense target for pulsed laser deposition (PLD) of thin films. Film growth was performed in 50 mTorr of O_2 within an ultra-high vacuum growth chamber using a KrF excimer laser operated at 248 nm on substrates held at either 600 °C or 750 °C. The $LaAlO_3$ (1 1 0) and $SrTiO_3$ (1 0 0) substrates used to promote epitaxial film growth were supplied by MTI Corporation.

Subsequent thermal processing of the $CaTi_{0.95}Pt_{0.05}O_{3-\delta}$ powder and films took place in a quartz tube within a tube furnace. For oxidation, dry air was flowed through the tube at 450 sccm. For reduction, 10% H_2 (balance N_2) was flowed through the tube at 100 sccm. These conditions mimic those in the previous work [1,2].

Cross-sectional STEM specimens of the processed thin films were fabricated by mechanical thinning and polishing on diamond lapping media and Ar-ion milling (Gatan PIPS, model 691) to electron transparency. It is worth noting that the film surfaces, along with any surface particles, are protected during fabrication by a layer of epoxy and a sacrificial silicon wafer. This is effective in preventing any specimen fabrication step from altering the morphology of the surface before observation. Specimens were examined in C_s-corrected JEOL JEM-2100F and JEM-2200FS STEMs operated at 200 kV. Electron energy-loss spectroscopy (EELS) spectra were acquired on a Cs-corrected JEOL JEM-ARM200F STEM with a cold-field emission gun operated at 200 kV. EELS quantification was performed with the Digital Micrograph software package. X-ray photoelectron spectroscopy (XPS) data were acquired using a Kratos AXIS Ultra DLD system with a monochromatic Al X-ray source.

3. Results and discussion

We begin with the powder samples of freshly-prepared Pt-doped perovskite, $CaTi_{0.95}Pt_{0.05}O_{3-\delta}$. (XPS revealed that Pt was present in the Pt^{2+} oxidation state as well as the Pt^{4+} state, based on data in the literature [8], leading us to allow for the likelihood of oxygen vacancies in this formula.) This powder was examined using C_s-corrected STEM. HAADF images provide atomic mass contrast, which allows us to directly identify small bright features as comprising relatively heavier Pt-rich clusters, confirmable by atomic resolution X-ray energy dispersive spectroscopy (EDS), contrasting against the lighter $CaTiO_3$ perovskite matrix. As shown in Fig. 1a, a few small Pt-rich clusters, several nanometers in diameter, are apparently present in the freshly-prepared material, which consists of roughly 100 nm-sized perovskite particles, which are predominantly single crystals. After reduction in 10% H_2/N_2 at 800 °C for 1 h, many more Pt-rich clusters appear, as shown in Fig. 1b. Based on through-particle focusing and sample rotation experiments (Figs. S1, S2 and Videos S1, S2, Supplementary material), most (~90%) of these Pt-rich clusters appear to be distributed uniformly throughout the $CaTiO_3$ matrix.

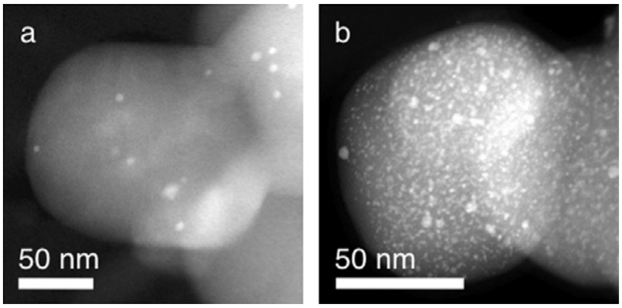

Fig. 1. HAADF images of Pt-doped perovskite, $CaTi_{0.95}Pt_{0.05}O_{3-\delta}$, particles (a) as freshly prepared and (b) after reduction in 10% H_2/N_2 at 800 °C for 1 h.

In order to learn more about the location of the Pt-rich clusters and their detailed structure, we next examined the thin films, grown specifically for cross-sectional STEM. The films were grown to thicknesses of order 100 nm, dimensionally similar to the perovskite powder samples produced in both this and the original work [2]. The as-deposited thin films were highly crystalline and epitaxial to the (1 1 0) $LaAlO_3$ substrate. Films grown at 600 °C exhibit a lamellar structure, with lamellae running along the [1 0 0] direction, as shown in Fig. 2a and b. While these lamellae are separated from each other by a network of micropores, they are aligned approximately along the same crystal directions, differing in in-plane orientation by only a slight rotation. It is important to emphasize that no pores were observed when cross-sectional specimens were viewed along the orthogonal in-plane direction. Films grown at 750 °C, in contrast, were smooth and dense as well as single-crystalline. Under close examination, all films appear to be homogeneous down to the atomic level, with no obvious segregation of Pt from the perovskite in the form of particles either on the surface or within. From this observation, coupled with the mechanics of PLD synthesis and corroboration from XPS confirming the ionic state of the Pt (Fig. S3, Supplementary material), it seems reasonable to assume that Pt sits on the expected b-site of the perovskite lattice.

A reduction treatment (800 °C, 10% H_2/N_2, 1 h) induces an amalgam of transformations within the thin films, as discussed briefly below. Chief among these is the formation of Pt-rich clusters (confirmed by EDS, as shown in Fig. S4, Supplementary material) within the perovskite matrix, appearing as bright contrast in Fig. 2c and e. As shown in Fig. 3a, these clusters are generally 1–3 nm in diameter, with many being clearly metallic, i.e., exhibiting the expected face-centered cubic (FCC) structure of Pt (Fig. S6, Supplementary material), but the smallest exhibiting ambiguous structure. The structurally ambiguous Pt-rich clusters may be either crystalline clusters that are not epitaxial with the perovskite, or they may be amorphous. Slightly larger clusters (3–5 nm) appear at extended defects, such as threading dislocations or $CaTiO_3$ rotation domain boundaries, with the largest on the free surfaces of the thin films, including the lateral lamellar surfaces, presumably due to faster diffusion of atomic Pt along these paths. It should be mentioned that similar observations were made on the films grown at 750 °C, with the exception that fewer Pt-rich clusters were found on free surfaces, presumably due to their lower area.

In addition, nanometer-size regions of the thin film, clearly associated with relatively large Pt-rich clusters inside the perovskite matrix, have transformed into crystal structures comprising primarily or exclusively Ti cations, most often identifiable as anatase TiO_2 due to both their crystal structure in the STEM micrographs (Fig. S7, Supplementary material) and their chemical composition by EELS, showing a high Ti signal to the exclusion of Ca. These regions, which collectively make up no more than a few percent of the volume of the film, generally form epitaxially