

In-situ observation of Rh-CaTiO₃ catalysts during reduction and oxidation treatments by transmission electron microscopy

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Daihatsu's 'intelligent catalyst' concept of a continuously self-regenerating three-way catalyst for automotive exhaust-gas treatment is based on the idea that a high dispersion of precious metal may be maintained through the combined effect of two opposing processes, precipitation and dissolution of precious-metal nanoparticles (NPs) that could occur for a precious-metal-doped perovskite oxide under the opposing influences of reducing and oxidizing gas conditions that exist during closed-loop feedback control of a typical gasoline-powered internal combustion engine [1]. Confirmation that such processes do, indeed occur in a variety of such systems under relatively extreme treatment conditions was originally provided by ex-situ x-ray absorption measurements, though little was revealed by these measurements about the kinetics of these processes or the resulting catalyst morphology. In order to learn something about the effect of the reduction and oxidation treatments on morphology [2], in-situ aberration-corrected scanning transmission electron microscopy (AC-STEM), combined with a novel electron-transparent gas cell [3] were employed to provide real time information about these processes in one of the 'intelligent catalyst' systems, Rh-doped CaTiO₃ (CTO).

The series of high-angle annular-dark-field (HAADF) images shown in Figure 1 provide an impression of the morphology evolution during the reduction and oxidation of the Rh-doped CTO powder. The CTO particles are generally 10-20 nm across, and some nanometer-size regions of brighter intensity, presumably due to Rh, already appear in the as-synthesized sample. When the temperature is raised to 600 °C in a reducing atmosphere (600 Torr of 4% H₂/Ar), these regions become clearer, and several more sub-nanometer-size regions become apparent (Fig. 1b). Fig. 1e shows an atomic-scale STEM image of the Rh-doped CTO in a reducing atmosphere. Upon subsequent heating to 600 °C in 600 Torr of pure O₂ (Fig. 1c), most of the smaller regions disappear within 10 minutes, and all are gone after 20 more minutes at 700 °C in 600 Torr of pure O₂ (Fig. 1d). In addition, two of the large regions of bright intensity appear to have coalesced (in the left CTO particle), and another appears to have gotten smaller (in the lower right CTO particle). Another demonstration of more cycles of reduction and oxidation is shown in Figure 2. Both reducing and oxidizing treatments were conducted in 600 Torr of forming gas (4% H₂ in Ar) and pure O₂, respectively, at 600 °C, and changes were observed to occur over several minutes of treatment time in each case. Here, however, significant changes in CTO particle size, shape, and arrangement were observed, in addition to the changes to regions of brighter intensity, as described before. Both the apparent sintering of CTO particles and a clear difference in the distribution of brighter intensity regions between this and a second reduction-oxidation cycle are apparent in the comparative images shown in Fig. 2. Another point of interest is that both transitions (changes in bright intensity

regions from first oxidation to second reduction and from second reduction to second oxidation) took place faster (within a minute) than in the initial reduction-oxidation cycle.

References:

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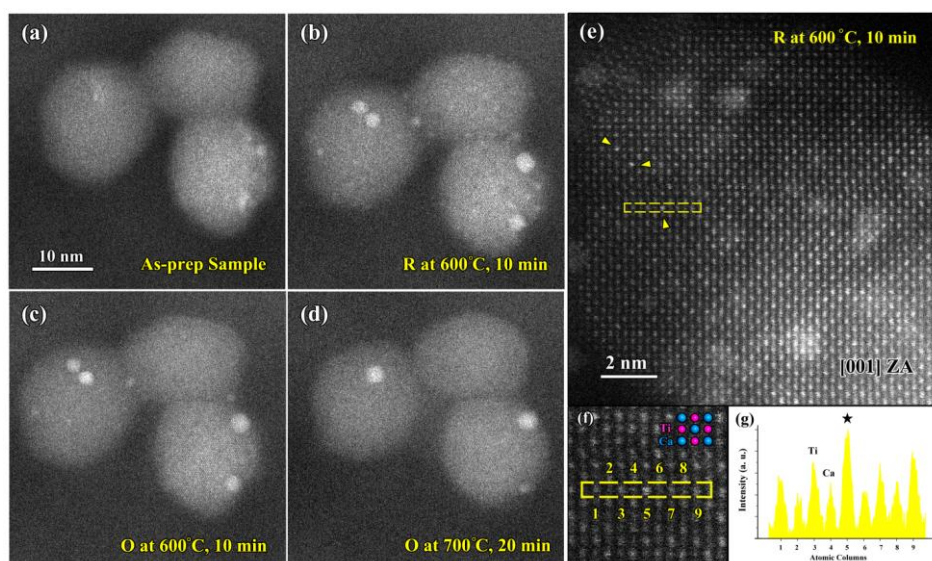


Figure 1. (a-d) In-situ HAADF images showing a full reduction-oxidation cycle of Rh-CTO powder at various temperatures and time lapses. (e-g) Atomic-scale in-situ HAADF image of Rh-CTO powder in 600 Torr of 4% H_2 /Ar.

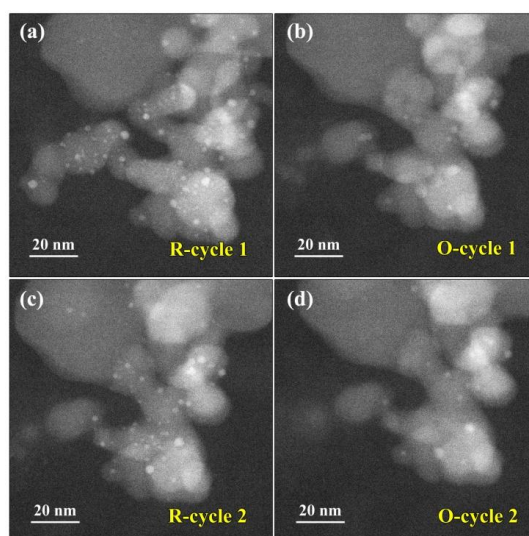


Figure 2. Comparison of HAADF images of Rh-CTO powder in 600 Torr of 4% H_2 /Ar (labeled by R) or pure O_2 (labeled by O) at 600 °C taken at the conclusion of the first (a, b) and second (c, d) reduction-oxidation cycles (labeled by 1 and 2).