

In-situ observation of Au/TiO₂ catalyst in Oxygen-Gas Environments

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Recently atomic structures of Au nanoparticles (NPs) / TiO₂ catalyst were discussed as a model catalyst of CO oxidation with high catalytic activity [1, 2]. The Au NPs / TiO₂ interfacial structures including light elements such as oxygen were observed by means of aberration corrected TEM [3], and were discussed in relation to the adsorption and/or activation of oxygen [1,4]. In addition, in-situ observations in gas environments are important in order to understand the structure in catalytic reaction process [5].

The substrate of TiO₂ was crushed from thin disk of single-crystalline rutile and Au NPs were deposited to its substrate in a HV chamber. The Au/TiO₂ specimen was mounted to a home-designed gas-injection holder, which were introduced to JEM-2100F microscope. The gas flow was controlled by a piezo valve and was kept constant by feedback from pressure gauge equipped in TEM column. The change of pressure between a high vacuum (HV) condition and gas environment was rapidly executed for ~ 3 sec.

Figure 1 shows a series of images; from HV condition (0 to 640 sec), through gas environment of O₂ at 100 Pa (640 to 1250 sec), to HV condition again (1250 to 1456 sec). No drastic change was observed in HV condition as shown in Fig. 1. On the other hand, the pillar without a lattice fringe grew around Au NPs in O₂ exposure at 100 Pa, and its shape drastically changed. The lattice fringe, whose period agreed that of TiO₂, was gradually formed in the pillar from O₂ exposure to HV condition. The growth of the pillar was clearly activated by O₂ exposure and the area of TiO₂ around Au NPs finally increased.

Figure 2 shows HAADF images and the corresponding core-loss spectrum of different Au/TiO₂ specimen. The EEL spectra were acquired from both regions with TiO₂ lattice and no lattice fringe. The signal ratio of O K-edge to Ti L-edge in no lattice-fringe region was much larger than that in TiO₂ lattice. These results suggest that the substrate around Au NPs changed to phase such as TiOx.

We propose a model for observation as shown in Fig. 1.

- (1) Oxygen is absorbed and activated at the Au/TiO₂ perimeter.
- (2) Ti cation diffused from substrate reacts the activated oxygen at the Au/TiO₂ perimeter.
- (3) The pillar of TiOx grows at the Au/TiO₂ perimeter and gradually changes to TiO₂.

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[2] M.S. Chen et al., *Science* 306 (2004) 252.

[3] T. Tanaka, K. Sano et al., *Proc. APMC 9 Meeting*, M11-08.

[4] Zhi-Pan Liu et al., *Phys. Rev. Lett.* 91 (2003) 266102.

[5] P. L. Hansen et al., *Science* 295 (2002) 2053.

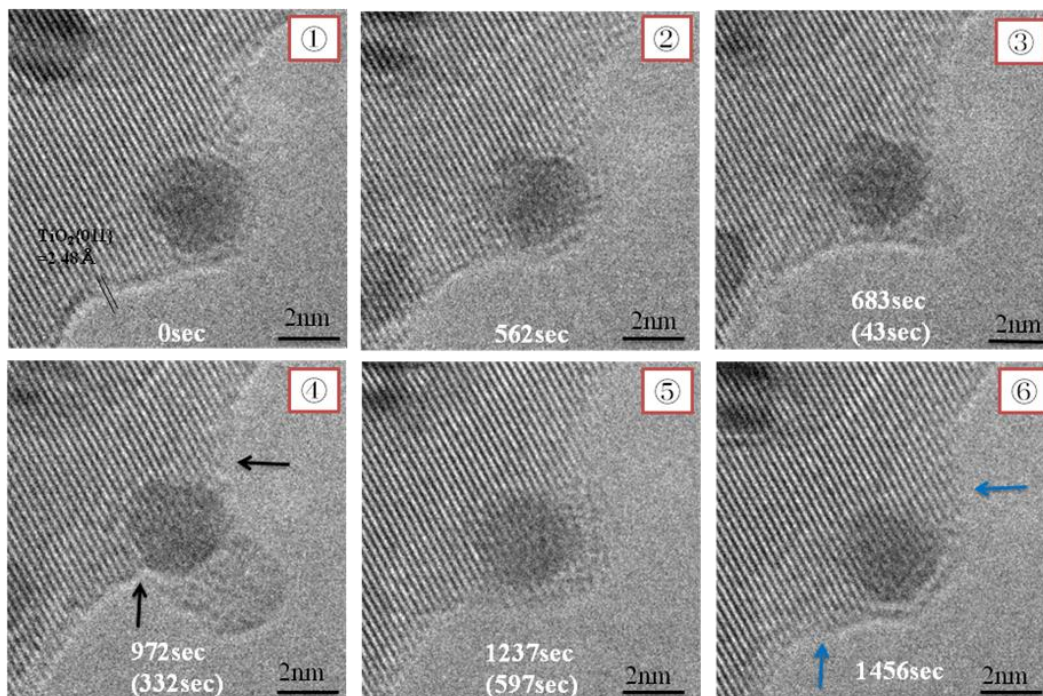
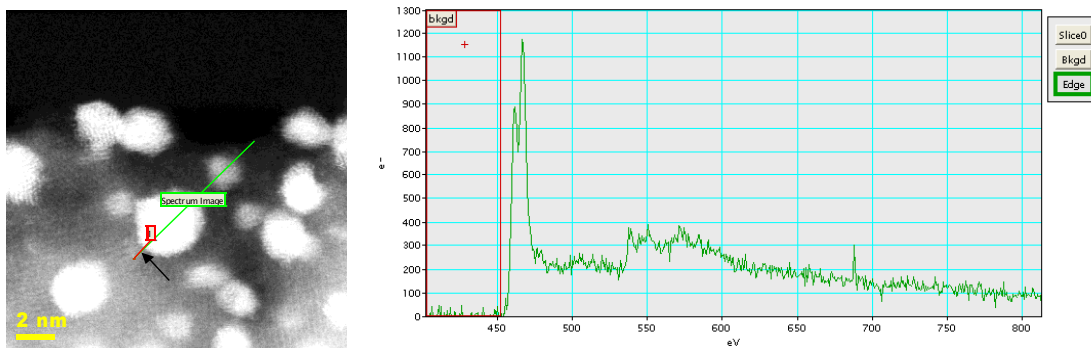


Figure. 1 In-situ experiments in high vacuum condition (0 to 640 sec), in O₂ gas environments at 100 Pa (640 to 1250 sec), and in high vacuum condition (1250 to 1456 sec).

(a) Rutile (TiO₂) lattice



(b) No lattice fringe (The same image as (a) with contrast emphasized)

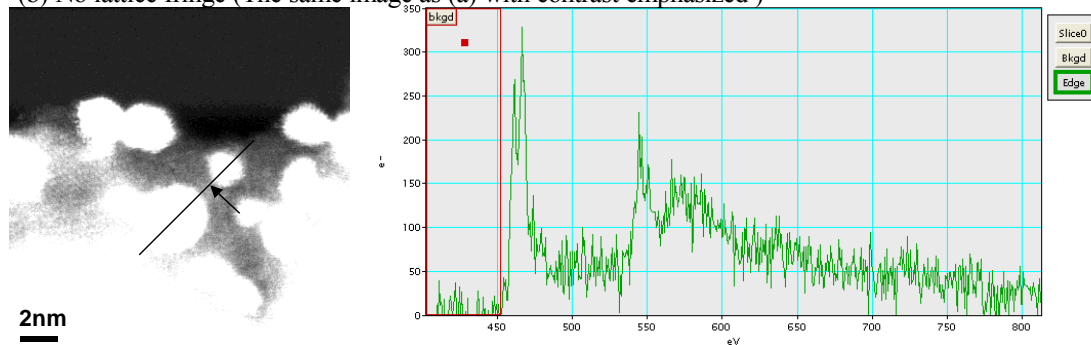


Figure. 2 HAADF image and corresponding core-loss spectra from the region with (a) TiO₂ lattice and (b) no lattice fringe, indicated by arrow. The ratio of O K-edge to Ti L-edge in (b) is greater than that in (a).