

In-situ ETEM Observation of Propene Epoxidation by Gold Nanoparticles Supported on Anatase TiO₂

Tadahiro Kawasaki^{1,2,3}, Hiroki Murase⁴, Kaname Yoshida¹, and Takayoshi Tanji^{2,3}

¹. Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya, Japan

². EcoTopia Science Institute, Nagoya University, Nagoya, Japan

³. Global Research Center for Environment and Energy based on Nanomaterials Science (GREEN), Tsukuba, Japan

⁴. Department of Electrical Engineering and Computer Science, Nagoya University, Nagoya

It has been well known that gold exhibits catalytic activity when it is in the form of fine particles having a size of less than several nanometers in diameter and is tightly supported on specific metal oxides [1]. One of the catalytic reactions the gold can perform is selective oxidation of propene (C₃H₆) to propene oxide (C₃H₆O), which is very important process in the chemical industry. Since the propene oxide (PO) has low vapor pressure (5×10^4 Pa @RT), the PO keep liquid form if surrounding pressure is controlled to be more than this value. Then we might be able to observe catalytic product PO in liquid form though it is almost impossible to visualize that in gas form. In this study, we have observed *in-situ* catalytic propene epoxidation on the gold nanoparticles supported on anatase TiO₂ by windowed-type environmental TEM, and have tried to clarify active sites of the gold catalyst by revealing product PO distribution.

Gold catalyst specimens were prepared by the deposition precipitation method, mixed with rod-shaped anatase TiO₂ powder. Our windowed-type E-cell [3-5] consisted of C/SiN hybrid membranes of 10 nm in thickness [3] assembled in a co-axial-type gas-flow specimen holder [5], that both we originally developed, was inserted into a conventional 200 kV TEM (H-8000; Hitachi). The reactant gas consisted of C₃H₆ (30%), O₂ (15%), traces of H₂O (0.1%), and N₂ (55%; for increasing pressure) was introduced at a pressure of $\sim 5 \times 10^4$ Pa.

Figure 1 shows TEM images taken at an interval of 5 minutes under gas atmosphere of only C₃H₆ at 6×10^2 Pa. There is almost no difference between two images. This means that propene gas with e-beam irradiation doesn't cause contaminations on the specimen. We have confirmed that the other gas molecules listed above also have negligible effects on the specimen surface. Fig. 2 are TEM images picked up from among the movie observed *in-situ* during the propene epoxidation reaction. Before starting the reaction, as shown in (a), the surface of Au and TiO₂ kept to be clean even in reactant gas of O₂, H₂O and N₂ because of no propene. In contrast, by adding propene gas to a pressure of 5×10^4 Pa, the product molecules started to be accumulated at the perimeter of interface between Au and TiO₂ substrate, as indicated by arrow-heads in Fig. 1(b) and (c). The reaction product disappeared in vacuum because surrounding pressure became lower than its vapor pressure (Fig. 1(d)). By increasing total gas pressure to 6×10^4 Pa, the product molecules were accumulated thicker and covered whole surface of the gold particle, as shown in Fig. 3(b), because higher pressure gas prevent the molecules from vaporization. These results indicate that the product should be considered as the PO molecules. They also directly proved that the active site where the catalytic reaction occurs is the perimeter of Au/TiO₂ interface, which is consistent with a model previously proposed [2] and experimental results in chemistry [6].

References:

- [1] M. Haruta, *Catalysis Today* **36** (1997), p. 153.
 [2] M. Haruta *et al*, *J. Catal.* **115** (1989), p. 301.
 [3] T. Kawasaki *et al*, *AMTC Letters* **4** (2014), p. 74.
 [4] T. Kawasaki *et al*, *Rev. Sci. Instr.* **80** (2009), p. 113701.
 [5] T. Kawasaki *et al*, *Microsc. Microanal.* **17**(2) (2011), p. 534.
 [6] T. Fujitani *et al*, *Angew. Chem. Int. Ed.* **50** (2011), p. 10144.

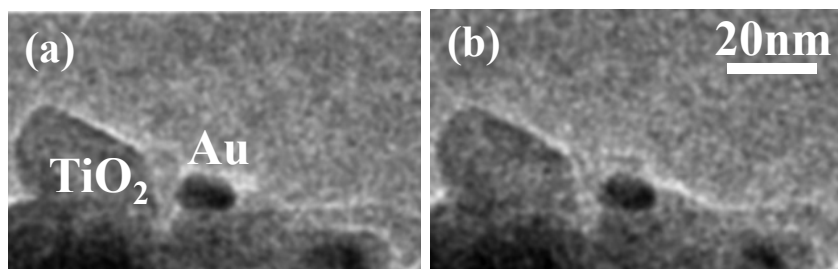


Figure 1. TEM images taken under propene gas condition. No contaminations are found on the specimen surface in both (a) initial condition and (b) after 5 minutes.

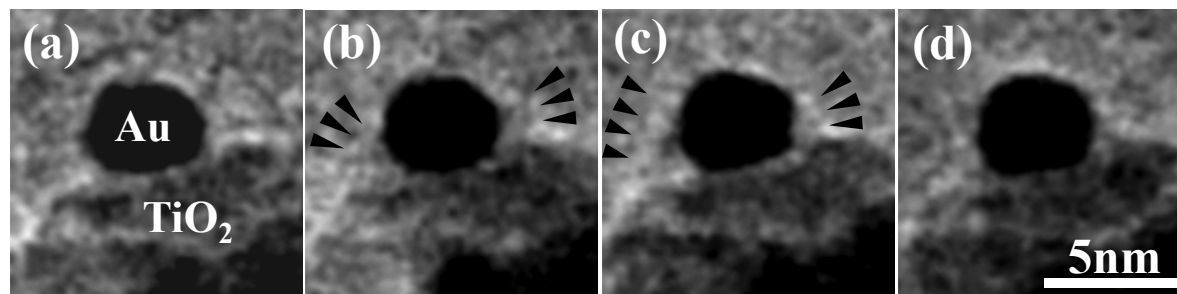


Figure 2. In-situ TEM images observed during propene epoxidation reaction. (a) Surrounding gas were O_2 , H_2O and N_2 (not reacted), (b) Propene gas were introduced at a total pressure of $\sim 5 \times 10^4$ Pa, (c) after 30 s from (b), and (d) in vacuum after gas evacuation.

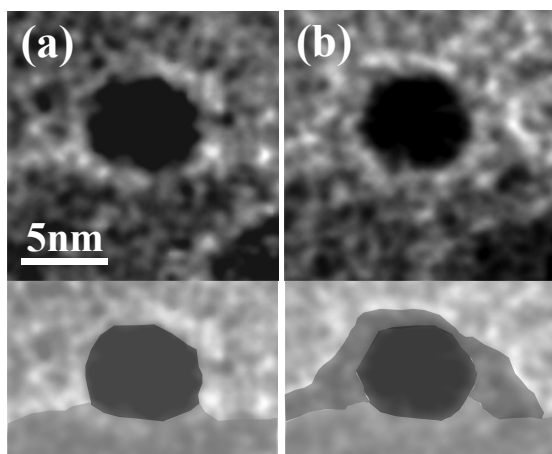


Figure 3. TEM images taken under higher gas pressure condition. (a) No propene gas (O_2 , H_2O and N_2), and (b) propene gas was added to a total pressure of 6×10^4 Pa.