Visualization of Reaction Site of Functional Material by Environmental TEM

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An environmental transmission electron microscopy (ETEM) is very powerful technique enabling to in-situ observation of functional materials, such as catalysts, battery electrodes/electrolytes, etc., immersed in gases, liquids, electric/magnetic fields and so on. One of the most important issues in the ETEM studies is to reveal working mechanisms of these materials. Especially for the catalysts, in order to understand their reaction processes, it is a key to determine the reaction sites on their surface, where product molecules are formed. In this study, we have investigated the reaction site of the gold nanoparticulate catalyst [1], which can perform the selective oxidation of propene (C3H6) to propene oxide (C3H6O) [2]. 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. In this condition, it might be possible to visualize the product PO molecules in liquid form, though it is almost impossible in gas form. Therefore, the reaction site can be determined by visualizing the PO formation on the catalyst surface with the windowed ETEM technique [3].

The specimens were gold nanoparticles supported on anatase TiO2, prepared by the deposition precipitation method. A windowed-type environmental-cell specimen holder, which is home-made system [4], was used in a conventional 200 kV TEM (H-8000; Hitachi). The reactant gas consisted of C3H6 (30%), O2 (15%), tiny amount of moisture (0.1%), and N2 (55%; just for increasing pressure) was introduced at a pressure of around 5 × 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 in advance that the other gas molecules listed above also have negligible effects on the specimen surface. Figure 2 shows 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 total 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 indicates 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/TiO$_2$ interface, as schematically shown in Fig. 4, which is consistent with a model previously proposed [1] and results in chemistry [2].

References

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

FIG. 2.
In-situ TEM images observed during propene epoxidation reaction. (a) Surrounding gas were O$_2$, H$_2$O 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), (d) in vacuum after gas evacuation.

FIG. 3.
TEM images taken under higher gas pressure condition of $6 \times 10^4$ Pa. PO molecules are covered on the catalyst surface (in red region).

FIG. 4.
Schematic illustration of reaction model of Au/TiO$_2$. 

C$_3$H$_6$ + O$_2$ + H$_2$O → C$_3$H$_6$O + Au

Anatase TiO$_2$