doi:10.1017/S1431927610058903
Microsc. Microanal. 16 (Suppl 2), 2010

In situ Observation of Au/TiO_2 Catalysts in Reactant Gases by Environmental Transmission Electron Microscopy

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Gold nanoparticles exhibit high catalytic activity when they are supported on selected metal oxides. Au/TiO_2 catalysts show great activity for CO oxidation even at low temperature [1]. Although it is well known that the catalytic activity of gold nanoparticles depends on the average size of them and support selection, the origin of the catalysis is still under debate [2]. Environmental transmission electron microscopy (ETEM) is useful to reveal the processes of reactions on nanoparticle catalysts [3, 4]. However, it is indispensable in ETEM observations to distinguish the effects of catalysis and those of electron irradiation. In this research, we observed Au/TiO_2 catalysts in reactant gases under electron irradiation with several different intensities.

An FEI Tecnai F20 transmission electron microscope equipped with an environmental cell was used for our observations. A differentially pumped system is adopted for the environmental cell, enabling us to perform high resolution observations in gases up to 2500 Pa (for N_2). Au/TiO_2 catalysts were prepared by the deposition precipitation method and show catalytic activity for CO oxidation below room temperature. For ETEM observation, Au/TiO_2 catalysts were dispersed over a carbon microgrid on a copper mesh. The mesh was set on a specimen holder and transferred into the ETEM operated at 200 kV. Figure 2 shows typical TEM images of Au/TiO_2 catalysts.

Figure 3 shows sequential ETEM images of a Au/TiO_2 catalyst in CO/Air ($CO:O_2:N_2$=1:21:78 vol%) at 100 Pa. Amorphous materials began to accumulate at the periphery of Au particles within one minute. Subsequently, some Au particles were lifted off and pillar-like structures were formed, and other Au particles were partially or completely encapsulated. Pillars and capsules often show the crystalline structures, which were identified as rutile-TiO_2 epitaxial to the support rutile-TiO_2. During the formation of pillars and capsules, Au particles were rotating and reconstructing the shape. To reveal the origin of these shape changes, we performed ETEM observations of Au/TiO_2 catalysts in high vacuum and pure O_2 gas with several different intensities of electron irradiation, considering the effects of electron irradiation on TiO_2 [5] and Au nanoparticles [6]. As a result, it is suggested that the formation of pillars and capsules are induced by two reactions: reduction of TiO_2 surface by electron irradiation and oxidation of Ti atoms or TiO_{2-x} by O_2 gas or residual oxygen at the periphery of Au particles. These effects must be taken into consideration in ETEM observations of Au catalysts.

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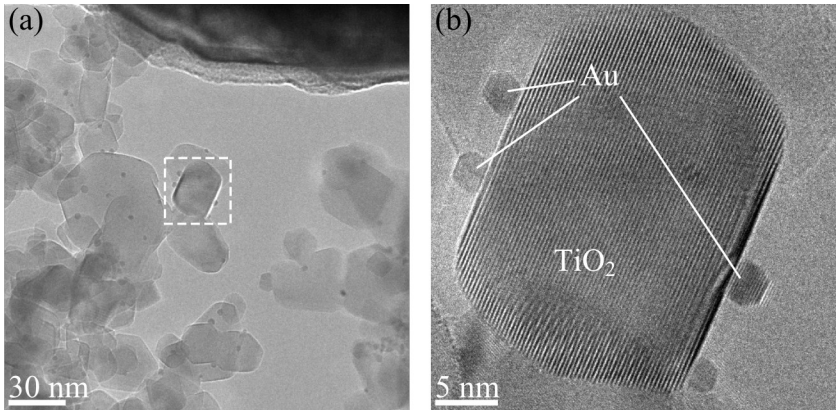

FIG. 1. (a) typical TEM image of Au/TiO_2 catalysts and (b) magnified image of (a).

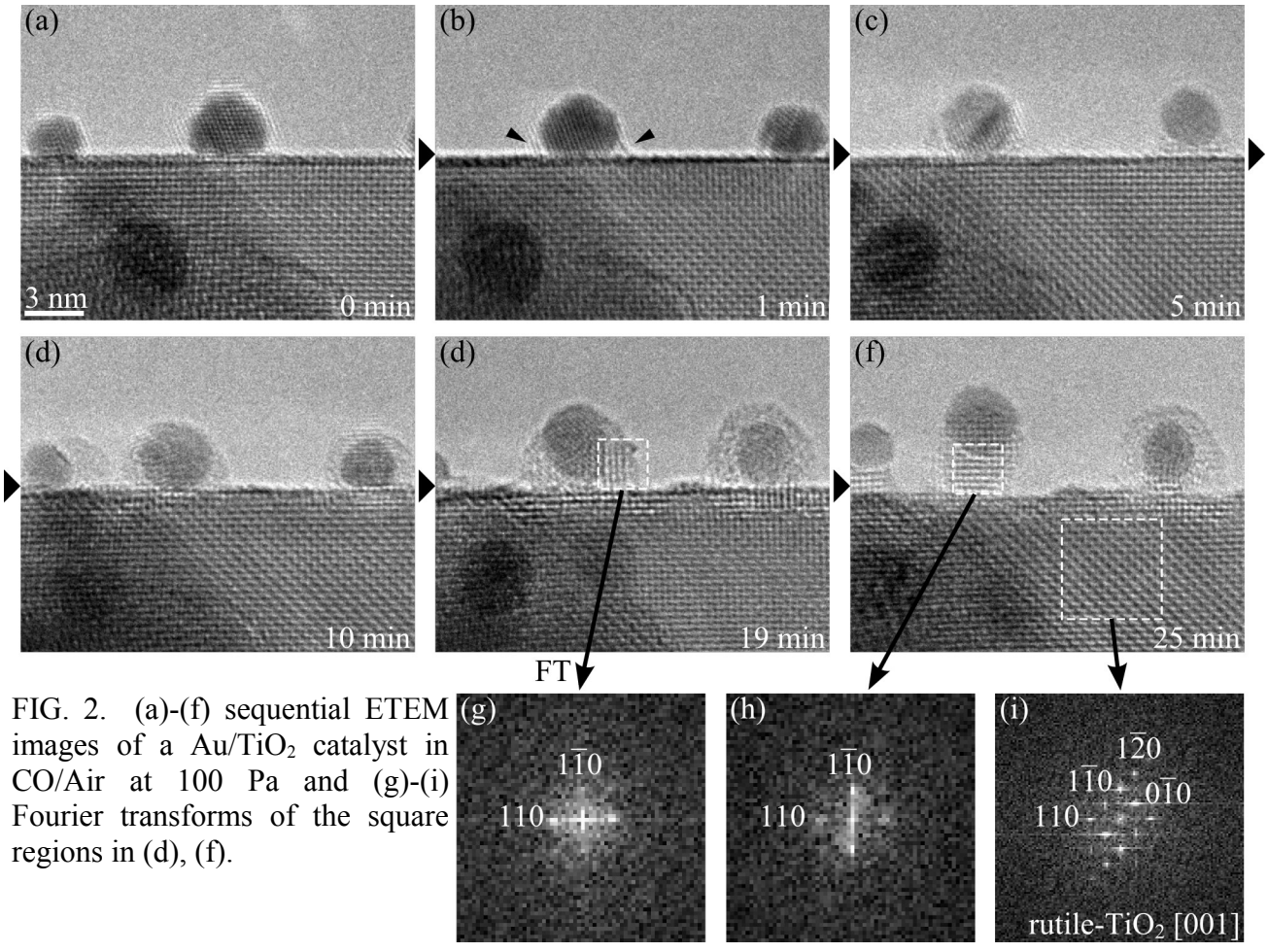

FIG. 2. (a)-(f) sequential ETEM images of a Au/TiO_2 catalyst in CO/Air at 100 Pa and (g)-(i) Fourier transforms of the square regions in (d), (f).

https://doi.org/10.1017/S1431927610058903 Published online by Cambridge University Press