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Dynamic TEM Observation of Gold Nanoparticles during Catalytic Reactions at Ambient Pressure

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It wad discovered that gold exhibits catalytic activity when it is in the form of fine particles having a size of less than 10 nm and is tightly supported on specific metal oxides [1]. In order to understand its catalytic behavior, *in-situ* observation under ambient reaction condition by environmental transmission electron microscope (ETEM) is quite essential [2-3]. The authors had revealed that the shape of catalytic gold nanoparticles is deformed during CO oxidation, even at relatively low gas pressure (500 – 1000Pa) [3-4]. In the paper, we report about *in-situ* observation of gold catalysts at up to ambient atmospheric pressure.

In our windowed-type environmental-cell system [5], a co-axial-type gas-flow specimen holder [6] with C/SiN hybrid sealing-films [7] is inserted into a conventional 200 kV TEM (H-8000; Hitachi). Dynamic TEM images were sequentially recorded using a CCD Camera (TVIPS; F114) for every 0.1 seconds with 12-bit grayscale level at 512×512 pixels. A gold catalyst was prepared by the deposition precipitation method, mixed with rod-shaped TiO_2 powder with an anatase structure as a support. The reaction gas consisted of 1% CO in artificial dry air [N_2 (78%) + O_2 (21%)]. The reaction may occur as $2CO + O_2 \Rightarrow 2CO_2$ on the catalyst surface. The total pressure of the gas was set at 10^3 - 10^5 Pa (atmospheric pressure).

Figure 1(a) – (h) shows a result of dynamic observation of a gold catalyst at $1x10^3$ Pa. They correspond to TEM images taken sequentially at intervals of 0.2 seconds. A gold nanoparticle is surrounded by white broke lines to emphasize its profile in each image. This result clearly show that the particle exhibited crystal habit and the surface mainly consists of (111), (100) and (110) facets. As an example, Fig. 1(i) corresponds to a schematic illustration of the Wulff construction of Fig. 1(h). In addition, the sequential observation revealed that the shape of the gold particle was changing during catalytic reaction. For quantitative analyses, tilt angle of the particle, and sizes of three facets and interface were measured in each images and were plotted in Fig. 2; the former was defined as an angle between the (100) facet and the substrate surface, and the latter was determined as total profile length of each facet and interface width (see Fig. 1(i)). The graph of Fig. 2 indicates that this particle wobbled randomly at the angle of $\pm$~10 degrees, and the sizes of (111), (110) facets were largely varied, though the interface width was almost constant. This means that there is strong connection between the gold and the TiO_2 substrate but shape of

the particle was easily fluctuated due to the heat-of-reaction of CO oxidation. Additionally, such structural variations were also dependent on surrounding gas conditions.

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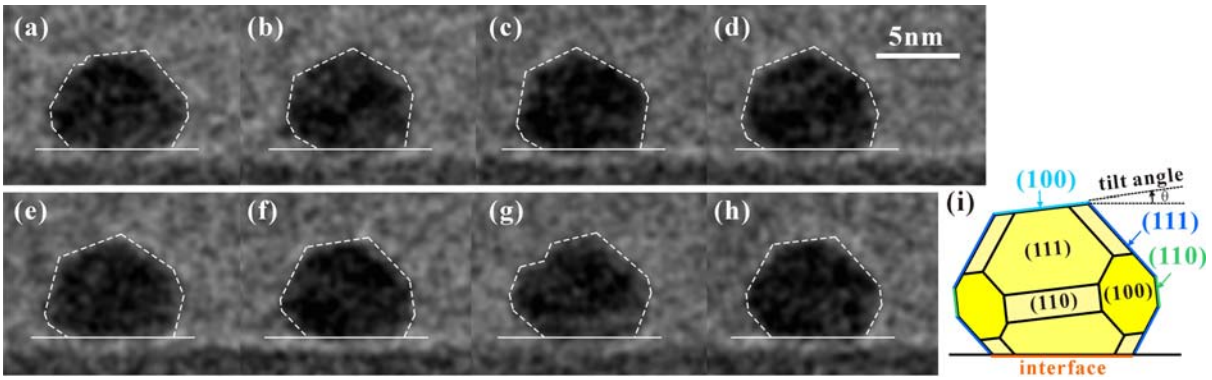

FIG. 1 (a)-(h) TEM images of an Au particle supported on TiO_2, observing under reaction gas condition (1000 Pa; CO + Air), taken at intervals of 0.2 seconds. (i) Illustration of Wulff construction of (h).

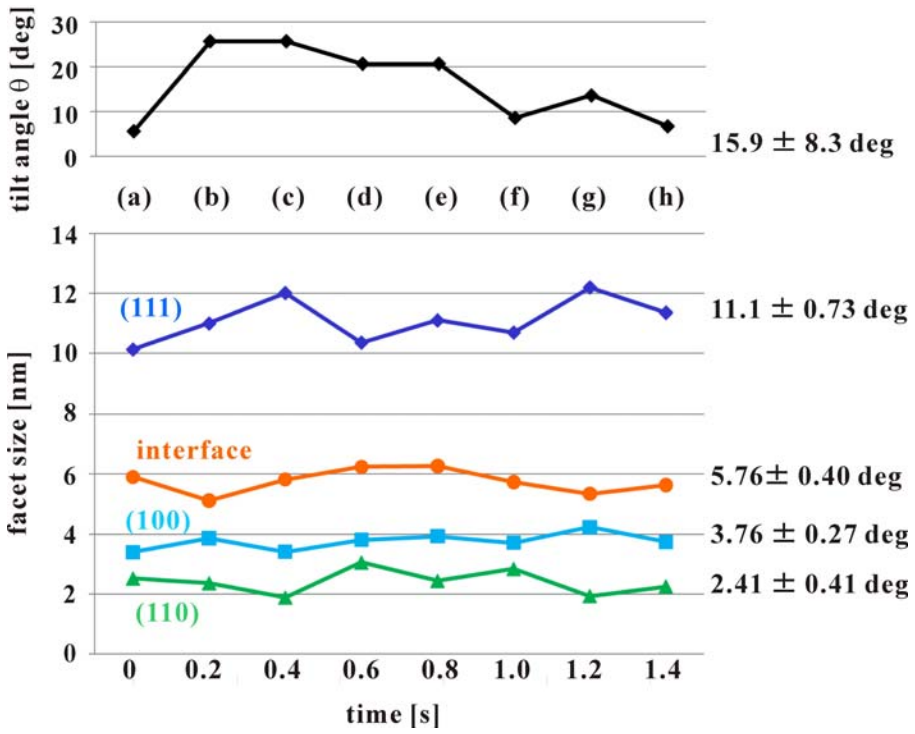

FIG. 2 Time-dependent changes of tilt angle of (100) facet (above) and sizes of three facets (below) of the Au particle measured in Fig. 1(a)-(h).

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