Size Dependency of Deformations of Catalytic Gold Nanoparticles Observed under Reaction Gas Environment

T. Kawasaki[1], T. Miura[1], Z. Cui[1] and T. Tanji[2]

[1]Dept. Electrical Eng., Nagoya Univ., Furo-cho, Chikusa-ku, Nagoya, 464-8603, Japan
[2]EcoTopia Science Inst., Nagoya Univ., Furo-cho, Chikusa-ku, Nagoya, 464-8603, Japan

It wad discovered that gold exhibits catalytic activity when it is in the form of fine particles having a size of less than ~ 5 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 size dependency of the deformations of the gold particles with the ETEM technique.

Gold catalyst specimens were prepared by the deposition precipitation method, mixed with rod-shaped TiO_2 powder (anatase structure) as a support. The reaction gas introduced to the specimen 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. Our windowed-type environmental-cell system [5] consisted of a co-axial-type gas-flow specimen holder [6] with C/SiN hybrid sealing-films [7] was inserted into a conventional 200 kV TEM (H-8000; Hitachi). Electron density irradiated to specimens was kept at 0.5A/cm^2 as low as possible to avoid the influence on the catalytic reaction during observations. Dynamic TEM images were sequentially recorded using a CCD Camera (TVIPS; F114) for every 0.2 seconds with 12-bit grayscale level at 512 × 512 pixels.

In order to evaluate deformations of each gold particle quantitatively, a parameter of “deformation value” was introduced. This parameter was determined by image processing as shown in FIG. 1; (1) Each image among the recorded movie was binarized to emphasize the shape of the particles. (2) Subtraction between adjacent binary images was performed to extract deformed part. (3) Area of the deformed part was measured and averaged among a series of the image. (4) Averaged value was divided by length of the outer perimeter of the particle to normalize the size effect, resulting in the “deformation value”.

FIG. 2 shows a graph of the deformation value *vs* the size of the gold particles, observing under CO oxidation condition. This result indicates that the deformation value increase dramatically when the particle size decrease less than 4 ~ 5 nm. Such peculiar size effect is also provided in a reaction rate (Turnover frequency; T. O. F.) of the gold catalysts [1]. By comparing them, these size dependencies are very similar. This means that the deformations of the gold particles we have observed with ETEM are strongly related to the rate of the catalytic reactions.

References
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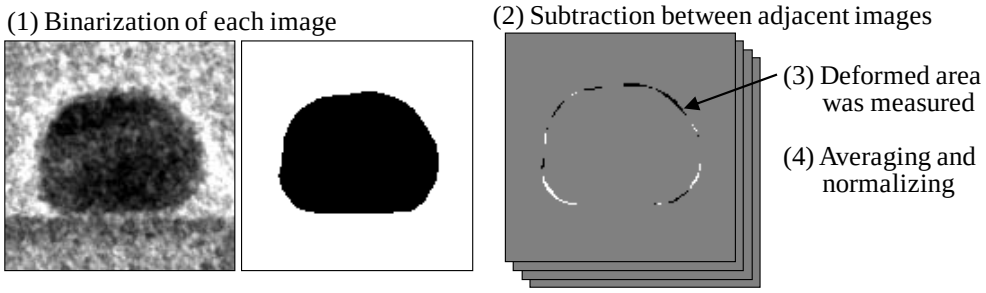

FIG. 1 Evaluation procedures of the deformed values in the series of the ETEM images.

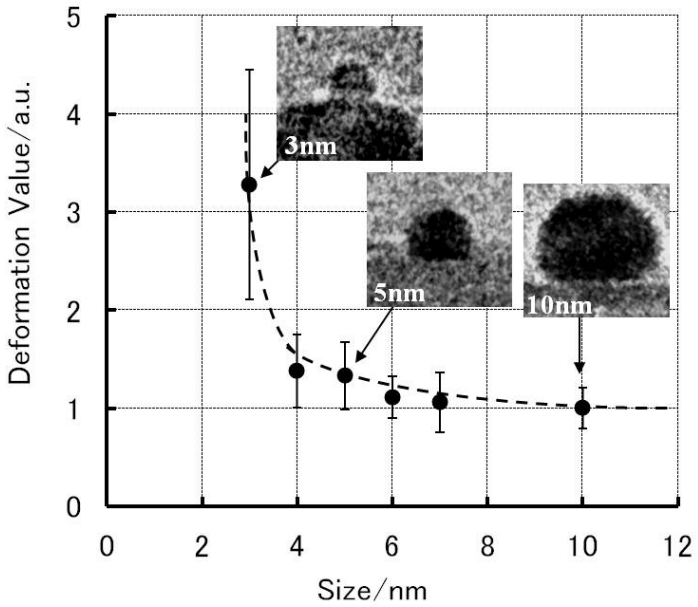

FIG. 2 Size dependency of the deformed value of gold particles, observing under reaction gas condition (1000 Pa; CO + Air).