Dynamic Observation of Gold Nano-particle Catalysts under Reaction Gas Environment by Transmission Electron Microscopy

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Abstract: The surface structure of catalytic gold nano-particles was dynamically observed for the first time during CO oxidation reaction by using a dedicated environmental-cell transmission electron microscope (E-cell TEM). Under the reaction environment, the shape of the particle was drastically changed, for example, facets on the gold particles dominantly disappeared and sometimes recovered. Since such surface shape changes became remarkable when the reaction gas pressure increased, it is predicted that this phenomena was caused by heat of reaction and may be related to the catalytic behavior.

Keywords: Gold nano-particle catalyst, In-situ observation, Transmission electron microscopy, Environmental-cell, Surface structure

1. INTRODUCTION

Gold exhibits remarkably high catalytic activity for some reactions, e.g. CO oxidation, 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 such as TiO₂, ZnO, and Fe₂O₃ [1-4] by specific preparation methods [3-6], even though bulk gold is chemically inert. This catalyst has unique properties that (1) its activity is quite dependent on the size of the gold particle; (2) reactions can happen are drastically changed by changing kinds of support metal oxides, even by changing crystal structures though having same composition. According to these results, M. Haruta et al., the discoverers of the phenomena, have predicted that the key of appearance of the catalysis is the interface between the gold particle and the support metal oxide, and its perimeter may be just the place where the reaction happens [3-4]. Therefore, it is very important to investigate the surface and the interface structures of the gold particle. Transmission electron microscopy (TEM), which is one of the most powerful techniques used to observe the atomic structure of such small particles, has been applied to observe fine catalytic particles of Pt, Rh, and so on [7-8]. Those of the gold have been also studied in detail by conventional TEM observations [9-11], and by spherical-aberration-free phase imaging [12-14]. The latter had revealed that atomic level structural deformations exist at the surface and the interface. However, such structural properties were all observed under “vacuum” environment, meaning that it is difficult to discuss the relationship between the observed structures and the catalytic behaviors directly. In order to bridge them, in-situ observation under “reaction gas” environment is quite essential. “Environmental-cell (E-cell) TEM” system [15-19], which enables gas introduction around specimens, is one of the indispensable methods for the above purpose. In the present paper, we report for the first time that the shape change of gold nano-particle catalysts happened during oxidation reaction, leading to demonstrate potentials of our developed E-cell TEM system.

2. EXPERIMENTS

Figure 1 shows a schematic diagram of our E-cell TEM system. This consists of two dedicated apparatuses, which are “E-cell specimen holder” and “gas control unit”, equipped with a conventional 200kV-TEM (H-8000, Hitachi). The former has a small room at its head, so called “E-cell”, for immersing specimens under the gas environment, connecting two pipes for the gas in/out. The E-cell is separated from vacuum in the TEM column with two ultra-thin carbon films set at the top and the bottom of the E-cell [17-19]. The films are most important components of this system, because they have to both withstand the gas pressure and pass the electron beam easily for avoiding deterioration of the resolution. We therefore improved a carbon deposition method to achieve < 10nm thick films, less than half of conventional ones, enabling to withstand more than 1-atom gas pres-
sure. This new ultra-thin film is one of the key points for high-resolution observation. In experiments, we successfully confirmed 0.24 nm resolution in the condition both upper and lower films existed (with no gas). The other developed apparatus is a gas control unit. This hand-made equipment, assembled by vacuum gages, a gas flow-meter, some valves, and stainless pipes, enables fine tuning of the pressure and the gas flow rate introducing from a reaction-gas tank. The after-reaction gas is evacuated by an oil-sealed rotary pump. The completed system realizes the catalytic reaction condition of the 1-atom gas atmosphere in the TEM column successfully. In-situ TEM images were sequentially recorded using a Fast Scan CCD Camera (TVIPS; F114) for every 1/5ths of a second with 12-bit grayscale levels at 1024 * 1024 pixels.

In the present experiment, the gold nano-particle catalysts were prepared by deposition precipitation (DP) method [4-6], supported on rod-shaped TiO2 powers having an anatase structure. The conditions of the DP method were adjusted so the size and loading of the gold particles were 3 ~ 5 nm and ~ 5 wt %, respectively. For TEM observation, the catalyst powders were supported on a perforated carbon film, called a micro-grid, and observed protruding into the micro-grid holes so that the TEM images were not disturbed by the background contrast caused by the carbon film. The reaction gas was CO content of 1% in dry air, which is reacted with O2 into CO2 on the catalyst surface. The pressure was set at two conditions, that are 0 - 151 Pa and 1000 - 1250 Pa, for investigating differences due to the gas pressure.

3. RESULTS AND DISCUSSIONS

Figs. 2 are TEM images picked up among the sequentially recorded ones. Here, a gold nano-particle is shown at the upper-right side of the images as black contrast, and a TiO2 support is observed below it as weak contrast. The dark part at the bottom of the images corresponds to the thick TiO2. “0 sec” (Fig. 2(b)) was determined as just the time to start introducing the reaction gas. Comparing Figs. 2(a) and (b), which were both observed under the vacuum condition at intervals of 5 sec, no differences are shown. This means that just the electron beam illumination induce no alteration of the gold particle. They had {111} and {200} facets at their tops in the vacuum, which is consistent with previous results [12-14]. These crystal habits, however, disappeared just after introducing the reaction gas, as shown in Fig. 2(c). After that, the surface structure of the gold was continuously changed. A semispherical shape is dominantly observed, e.g. Figs. 2(d) and (f), which correspond to the image taken under 22 Pa and 151 Pa, respectively. It is, on the other hand, quite interesting that the before-reaction shape having the same crystal habit with Figs. (a) and (b) sometimes recovered, as shown in Fig. 2(e) (68 Pa). Additionally, a significant phenomenon was observed. Structural deformation happened even when the gold particle was courted by a certain material, as indicated by arrowheads in Fig. 2(a), which is considered to be major contamination of H2O. In such a case, it should be generally believed that gas molecules couldn’t be reached onto the catalyst surface, resulting in no reactions. However, the present result is not invalid because it was previously discovered that the catalytic activity of the gold nano-particles increases by existing moisture [20] although that of the other catalysts decreases due to the above reason. This indicates that H2O on the gold surface doesn’t disturb procedure of the catalytic reaction, rather accelerate it. Its mechanism is not clear at the present, which the reaction gas molecules will adsorb on the H2O layer or will penetrate through the layer into the gold surface. It should be noted that gradually decreasing of the courted layer on the gold was often observed during the reaction in the other cases, predicting that H2O on the catalyst surface may provide oxygen atoms for the CO oxidation, or may vaporize by heat of reaction as mentioned in the next paragraph.

Figs. 3 show in-situ images observed under the reaction gas environment. The gas pressure increased gradually from 1000 Pa to 1250 Pa, which correspond here to “0 sec” and “22 sec” in terms of time, respectively. A gold nano-particle is at the center of the image and a TiO2 support is at its lower half. Owing to high gas pressure,
image quality is considerably deteriorated in comparison with that of Figs. 2. However, sequential shape change of the gold particle is clearly shown. It is very important here that the shape change is more remarkable than that in the case of the low gas pressure of Figs. 2. For example, the gold particle in Figs. 3(b) - (c) and Figs. 3(d) - (f) was shown as considerably different shapes, although they were observed at quite short intervals of 0.4 sec and 0.6 sec, respectively. This indicates that the reaction gas pressure affects deformation speed of the gold particle. Since higher gas pressure leads to more number of reacted gas molecules, it should be considered that driving force of the shape change of the gold might be heat of reaction produced by the CO oxidation. According to the previous investigation [21], reducing the size of metal particles causes reducing their melting points, e.g. 573K in the case of the 2nm-sized gold particle. This means atomic structure of the small sized particles easily deformed by the effect of heat, which supports the above hypothesis. Note that the shape changes had happened around the top of the particle and no deformation had been shown around its interface, as well as no displacement of the particle. This result proves that remarkable strong connection between the gold and the TiO₂ support exists. Such a nature had been already discovered [1-4], as is one of the indispensable conditions of appearance of the catalytic activity. However, the present result newly reveals that it has been kept during the reaction even under the condition that the particle itself is considerably deformed.

4. CONCLUSION
The dedicated E-cell TEM system is quite effective to observe the dynamic behavior of the gold nano-particle catalyst during the reaction. In-situ investigation using this system clearly illustrated for the first time that the shape of the gold particles was different from that observed under the vacuum condition, and was continuously deformed. They dominantly showed the semispherical shape and sometimes exhibited the crystal habit having some facets on the surface. The speed of the deformation was influenced by the reaction gas pressure around the specimen, that is higher gas pressure produced more remarkable alteration. This indicates that the driving force of such deformations might be heat of reaction, but relationship to the appearance of the catalytic activity of the gold is not clear in detail at the present. In order to reveal it, simulations based on physics, e.g. the first principle calculations, are very powerful [22-24], because they can yield the physical property information from the structural information. From such a point of view, the present results are more significant than the previous ones taken under the vacuum conditions. It is now declared that just the in-situ analyses provide actually important data as far as in the case of the gold catalysts. Development of the present E-cell TEM system to make the higher resolution will represent alterations of atomic structure at the gold surface and especially at the interface between the gold and the support materials. This will make the mechanism of the gold catalyst clear by combining with the physical simulations in the near future.

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