Migration of Au Nanoparticles on a TiO$_2$(110) Surface in Reactant Gases Observed by In-Situ STM at Elevated Temperatures

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Behavior of Au nanoparticles on a TiO$_2$(110) cross-linked (1×2) surface under the atmosphere of reactant gases (CO, O$_2$, CO+O$_2$) at elevated temperatures was observed by scanning tunneling microscopy (STM). Au nanoparticles were grown larger by the thermal treatment in O$_2$ or O$_2$+CO atmosphere. In-situ STM in such oxidative atmosphere revealed that the migration of Au nanoparticles occurs associated with the oxidation of a TiO$_2$ surface from cross-linked (1×2) to (1×1) structure. These results imply that the Au–Ti interaction is made unstable in real atmosphere of catalytic reactions, even if the unsaturated Ti species act as the initial nucleation sites.

Keywords: Scanning tunneling microscopy; Nano-particles; Gold; Titanium oxide; Catalysis

I. INTRODUCTION

Since Au is chemically very stable and it does not lose metallic luster even after long term exposure to air, Au had been regarded as being catalytically inert. However, in 1987, Haruta and co-workers have discovered that Au nanoparticles, supported on metal oxides, exhibit novel catalytic activity such as low-temperature CO oxidation [1]. The mechanism to activate even Au should include an important principle to develop nano-structured catalysts. However, the details are still unclear.

The catalytic activity of Au is strongly dependent on the particle size and the kind of metal-oxide supports, which suggests that the nano-sized interface between Au and supports plays an important role for the activity [2, 3]. In order to clarify this nano-hetero interface effect, experimental and theoretical researches have been performed on Au/TiO$_2$ model catalysts [4, 5], and revealed that the interaction between Au and a stoichiometric ideal TiO$_2$ surface is rather weak, while Au is adsorbed strongly on surface oxygen vacancies [6–9]. From such results, it is proposed that oxygen vacancies activate Au nanoparticles through charge transfer, orbital hybridization or structural deformation.

On the other hand, our group has examined various stoichiometries of TiO$_2$ surfaces by first-principles calculations. Especially, we pointed out the importance of an oxygen-rich surface for the strong Au-support interaction [10–12]. Recently, detailed scanning tunneling microscopy (STM) analyses experimentally proved the strong interaction between Au and an oxygen adatom [13–16]. These results imply the importance of the oxygen-rich surface rather than oxygen vacancies under the realistic condition of catalytic reactions (i.e. oxidative atmosphere).

To examine the influence of the surface stoichiometry condition, we investigate the behavior of Au particles on a TiO$_2$(110) cross-linked (1×2) surface under UHV and under the atmosphere of reactant gases (CO, O$_2$, CO+O$_2$) at elevated temperatures by using STM. Results revealed that Au nanoparticles start to migrate associated with the surface oxidization by the atmosphere of reactant gasses, indicating that the Au–Ti interaction is not stable under the conditions of catalytic reactions or catalyst preparation.

II. EXPERIMENTAL

All experiments were performed in a UHV-STM system (JSTM-4500XT, JEOL) with a base pressure of 2×10$^{-8}$ Pa. Substrates were polished TiO$_2$(110) single crystals. The cross-linked (1×2) surfaces were obtained by repeated cycles of Ar$^+$ sputtering (3 keV, 5–10 min) and annealing (800°C, 10-30 min). Gold was deposited by vacuum evaporation with the substrate being kept at room temperature. Typical amount of Au was 0.03–0.07 ML. Note that coverage was estimated from the apparent height of Au nanoparticles observed in STM images, and one monolayer (ML) was defined as the packing density of a Au(111) plane, 13.9 atoms/nm$^2$. High purity grade O$_2$ and CO gases were used without any refining. These were introduced into the vacuum chamber through a variable leak valve. STM observation was performed in constant current mode. Typical values of sample bias voltage and tunneling current were 1.0–1.5 V and 0.03–0.1 nA, respectively. The obtained images were processed by using WSxM software [17]. The height of the Au nanoparticles was semi-automatically measured from the STM images using an original macro in ImageJ software. In the macro, “substrate surface beside the particle” is set to the position where the incline is zero. Experimental details have been described in the previous reports [18, 19].

III. RESULTS AND DISCUSSION

The oxidation of the cross-linked (1×2) surface was confirmed with the UHV-STM. Below 200°C, the surface oxidization was not observed at the O$_2$ pressure of 1×10$^{-4}$ Pa. At 400°C, the cross-linked (1×2) structure was oxidized into the (1×1) structure at the O$_2$ pressure of 5×10$^{-6}$ Pa. These results are consistent with previous papers [20, 21].

The growth of Au nanoparticles on a cross-linked (1×2) surface was investigated by annealing in UHV, CO, O$_2$ and CO+O$_2$ mixture at 400°C. Figure 1 shows (a-d) STM images using an original macro in ImageJ software. The oxidation of the cross-linked (1×2) surface was confirmed with the UHV-STM. Below 200°C, the surface oxidization was not observed at the O$_2$ pressure of 1×10$^{-4}$ Pa. At 400°C, the cross-linked (1×2) structure was oxidized into the (1×1) structure at the O$_2$ pressure of 5×10$^{-6}$ Pa. These results are consistent with previous papers [20, 21].

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FIG. 1: STM images of Au nanoparticles on a TiO$_2$(110) surface treated at 400$^\circ$C for 120 min in (a) UHV, (b) CO, (c) O$_2$ and (d) CO+O$_2$. The partial pressure of CO and O$_2$ was 5×10$^{-6}$ Pa. The STM images were taken at room temperature with the bias voltage of 1.5 V and the tunneling current of 0.05-0.1 nA. (e) A plot of the average height of Au nanoparticles, treated at 400$^\circ$C in UHV, CO, O$_2$ and CO+O$_2$, as a function of annealing time. The cross-link site anchors the particle and prevents the particle growth. This is consistent with our previous result that a cross-link site acts as a stable adsorption site below 400$^\circ$C [19]. The particle growth by annealing in CO is also small (< 1%), and the surface maintained cross-linked (1×2) structure as shown in Fig. 1(b). That is, the cross-link site acted as an effective anchor site, even in CO atmosphere.

On the other hand, the particle height increased greatly by annealing in O$_2$ (Fig. 1(c)). After 120-minutes annealing, it increased by about 60%. Moreover, the cross-linked (1×2) structure disappeared, and the surface structure was almost changed to the (1×1) structure. We observed similar topological change in CO+O$_2$ mixture (Fig. 1(d)): the surface structure was also changed to the (1×1) structure, and the particle height increased by about 50%. These results indicate that oxidation of a TiO$_2$ surface from cross-linked (1×2) to (1×1) strongly influences the growth of Au nanoparticles.

In order to clarify the relation between the surface oxidation and the particle migration, in-situ observation was performed at 400$^\circ$C in oxygen environment. After stabilizing the thermal drift at 400$^\circ$C, we introduced the O$_2$ gas of 5×10$^{-6}$ Pa into the STM chamber. Figure 2 shows a series of STM images obtained at the same position. At twenty-three minutes after the introduction of O$_2$, the cross-linked (1×2) structure still remained, and Au particles stayed at the initial position. It should be noted that structural change in this in-situ observation was slower than that shown in Fig. 1. We consider the possible reason to be the reduction of O$_2$ pressure or substrate temperature by the tip scan. With the increase in annealing time, the cross-linked (1×2) structure was oxidized into the (1×1) structure. In response to this oxidation, the tip images obtained after 120-minutes annealing, and (e) a plot of the average height of the Au nanoparticles as a function of annealing time. Pressure of CO and O$_2$ was 5×10$^{-6}$ Pa, and partial pressure of CO and O$_2$ in CO+O$_2$ was also 5×10$^{-6}$ Pa. The STM observation was performed at room temperature, and the samples were repeatedly annealed and observed. To obtain average height, 39-207 particles were analyzed for each data point in (e), and their standard deviations were ranged from 0.13 to 0.24 nm.

When the particles were annealed in UHV, significant structural change was not observed. The particle height slightly increased by about 10% after 120-minutes annealing. As shown in Fig. 1(a), the Au nanoparticles were mostly adsorbed on the cross-link sites, indicating that
scan became unstable and some particles suddenly moved during the scan. Then, after 78 minutes, many particles moved from their initial positions.

Figure 3 shows magnified images of the square area shown in Fig. 2. The relation between the surface oxidation and the particle migration is clearly understood by the motion of the particle indicated by an arrow. After 60-minutes annealing, the surface beside the particle was oxidized into the (1×1) structure, and the particle stayed at the initial position. After 74 minutes, the initial adsorption position of the particle was surrounded with the (1×1) structure completely, and the particle moved to the domain boundary between the cross-linked (1×2) and the (1×1) structure.

Oxygen-induced particle growth of Au on TiO$_2$(110)-(1×1) has been reported by Lai et al. [22]. They proposed the Au-atom transport accelerated by O species activated on Au nanoparticles. If such active oxygen is supplied, oxidation around the particles should preferentially occur. However, such phenomenon was not observed. Instead, our results showed the migration of the Au nanoparticles follows the surface oxidation from the cross-linked (1×2) to the (1×1) structure. This is caused by the disappearance of stable anchor sites (i.e., cross-link sites) and the weak interaction between Au and the (1×1) surface.

For the previously believed model, in which oxygen vacancies activate the catalysts, Au–Ti bonds should be stable under oxidative condition. A cross-link site includes unsaturated Ti species, which stabilize Au particle via Au–Ti bonding like an oxygen vacancy. However, our results imply that the Au–Ti bonds are broken through the oxidation of the TiO$_2$ surface.

IV. CONCLUSION

The STM observation of the Au nanoparticles on the TiO$_2$(110) cross-linked (1×2) surface in the reactive gases at the elevated temperatures revealed that migration of Au nanoparticles is strongly influenced by the surface oxidation from cross-linked (1×2) to (1×1) structure. This implies that the Au–Ti interaction is made unstable under realistic reaction or preparation condition (at high oxygen pressure), even if the unsaturated Ti species act as the initial nucleation sites. We consider that our results support the model in which oxygen vacancies have less importance than an oxygen-rich surface for real catalyst systems.

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