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Analytical TEM study on structural changes of Au particles on cerium oxide using a heating holder

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Abstract

The structure changes of Au nano-particles supported on CeO_2 were observed by using an analytical transmission electron microscope (TEM) with a specimen heating holder. The disintegration and growth of Au particles on CeO_2 were successfully observed in the atomic scale. In situ observation of Au particles at elevated temperature reveals that the Au particles on CeO_2 grow by Ostwald ripening process through surface diffusion. Iridium particles on CeO_2 were also observed during the heating process for comparison. The growth mode of Au particles is quite different from that of Ir.

Keywords: Au; CeO_2; TEM; Diffusion

1. Introduction

Gold nano-particles on CeO_2 are of great interest since the Au/CeO_2 catalyst is applied for various catalytic reactions [1–4]. It was reported that the Au/CeO_2 catalysts show high catalytic activity for low-temperature water gas shift reaction and CO oxidation [1–3]. The Au/CeO_2 catalysts prepared using the deposition precipitation method also show high catalytic activity for the oxidative decomposition of volatile organic compounds [4]. Recently, it is reported that atomically dispersed small Au clusters, positively charged on a CeO_2 surface, are responsible for low-temperature water gas shift reaction or CO oxidation [5,6]. Thus, it is important to examine the size and structure of Au particles on CeO_2 precisely with an atomic scale to understand the catalytic activity. The structure of the Au/CeO_2 catalysts was observed using an analytical transmission electron microscope (TEM) in our previous work [7–9]. Annular dark field scanning transmission electron microscopy (ADF-STEM) and energy dispersive X-ray spectroscopy (EDS) revealed that Au particles smaller than 2 nm in diameter are highly dispersed on the CeO_2 support [7] while conventional TEM observation could not reveal the small Au particles. TEM observations were also performed on a model catalyst sample that was prepared using the powder of larger CeO_2 grains with lower surface area and low index facets in order to study the Au/CeO_2 interface. And preferential orientation relationship between Au and CeO_2 crystals was observed by high resolution TEM (HRTEM). During the observations, we further found novel structural changes of Au particles on CeO_2 crystals [8,9]. Gold particles rapidly shrink layer by layer down to Au monolayers on CeO_2, and the particles recover if the electron beam is turned off. It was deduced that such structural changes of Au particles depend on the changes in the oxidation state or the density of oxygen vacancies in a CeO_2 support induced by the electron beam irradiation. Although the inclement of temperature by the electron beam should be also an important factor for such structure changes, it was difficult to estimate local temperature at observation area.

In the present work, we examine the effect of temperature on the structure changes of Au particles on CeO_2. We developed a new specimen heating holder in order to perform in situ TEM observations at elevated temperature. The growth process of Au particles by heating is important to understand the preparation

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and degradation processes of the catalysts. We have successfully observed the behavior of Au particles and CeO_2 in the atomic scale during heating. We have also examined the behavior of Ir particles in the Ir/CeO_2 catalyst [7] for comparison.

2. Experimental

The specimen heating holder was newly constructed for in situ TEM observation of diffusion and growth process of metal particles on metal oxide supports. The direct heating method by a tungsten filament, developed by Kamino and Saka [10], was adopted. The temperature was calibrated for the heating current of the tungsten filament by pyrometer in a substitute vacuum chamber. Thus, the estimated temperature includes a substantial error for low temperature region below 800 K. A JEOL JEM-3000F transmission electron microscope was used with an accelerating voltage of 300 kV. The electron energy loss spectroscopy (EELS) measurement was also performed by Gatan Imaging Filter (GIF). The spectra were obtained in 2–4 s. TEM images were recorded by a video tape recorder or hard disk recorder through Gatan TV camera. Some TEM images were also recorded by a CCD camera of GIF.

The Au/CeO_2 and Ir/CeO_2 model catalysts were prepared by the deposition precipitation method [11]. Gold nano-particles were deposited on commercially produced, high-purity CeO_2 powder (Kojundo Chemicals Lab. Co., purity 99.99%) using the deposition precipitation method, which is useful for the preparation of highly dispersed Au particles on metal oxide. CeO_2 grains were dispersed in a suitable volume of aqueous solution of $HAuCl_4$ at a fixed pH of 7. The Au content of the solution was 5.0 wt% with respect to the weight of CeO_2 grains. The dispersion was aged at 343 K for 1 h and washed with distilled water several times. The solid material was then vacuum-dried at 0.4 Pa for 15 h at room temperature and calcinated at 673 K in air for 4 h. The Ir/CeO_2 sample was also prepared similarly using aqueous solution of $IrCl_4$. The powder of Au/CeO_2 and Ir/CeO_2 were directly supported on the tungsten filament of the specimen holder without solvents.

3. Results and discussion

Fig. 1 shows typical TEM images of the Au/CeO_2 catalyst during the heating process from room temperature to 1230 K. The images were recorded by a CCD camera. The drift of the sample occurred during the heating, but the high resolution images resolving 0.235 nm corresponding to the Au(1 1 1) lattice space were recorded within 1 s at each temperature. Hemispherical Au particles about 3–5 nm in diameter are observed on the surface of a polyhedral CeO_2 support at room temperature. Small Au particles indicated by an arrow in Fig. 1a disappear during the heating process from 670 to 770 K as shown in Fig. 1b. All the Au particles disappear at 1000 K in Fig. 1c. It can be said that small Au particles disappear below the melting point of bulk Au (1337 K). The shape of the CeO_2 support also changes at the temperature over 1000 K. The facet of the CeO_2 crystal is also lost and the polyhedral shape becomes round one. During the heating process, the Au particles completely disappear, and there remains no Au monolayer on the CeO_2 surface. The latter point is quite different from our previous experiments under electron beam irradiation without heating [8,9]. The recovery of Au particles after exposure to air is also not observed, differently from our previous experiments.

Fig. 2 shows the O-K edge (Fig. 2a) and Ce-M edge (Fig. 2b) of EELS spectra obtained from CeO_2 at each temperature during the heating process. The oxidation states clearly appear in EELS spectra [12], as observed in previous experiment [9].

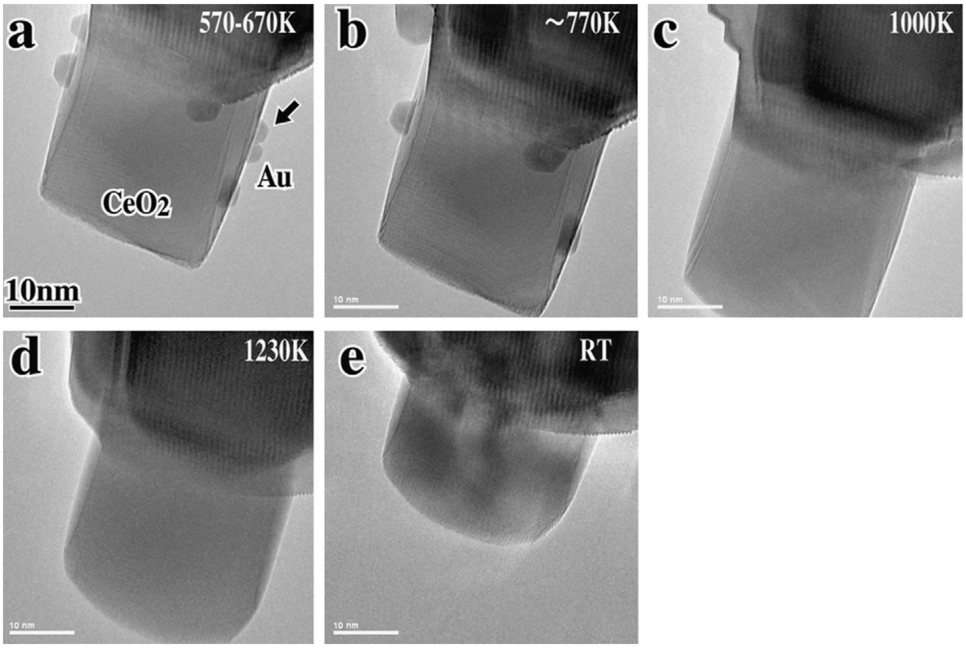

Fig. 1. A successive series of TEM images of Au particles on CeO_2 during heating at: 570–670 K (a), 770 K (b), 1000 K (c), 1230 K (d) and room temperature (e).

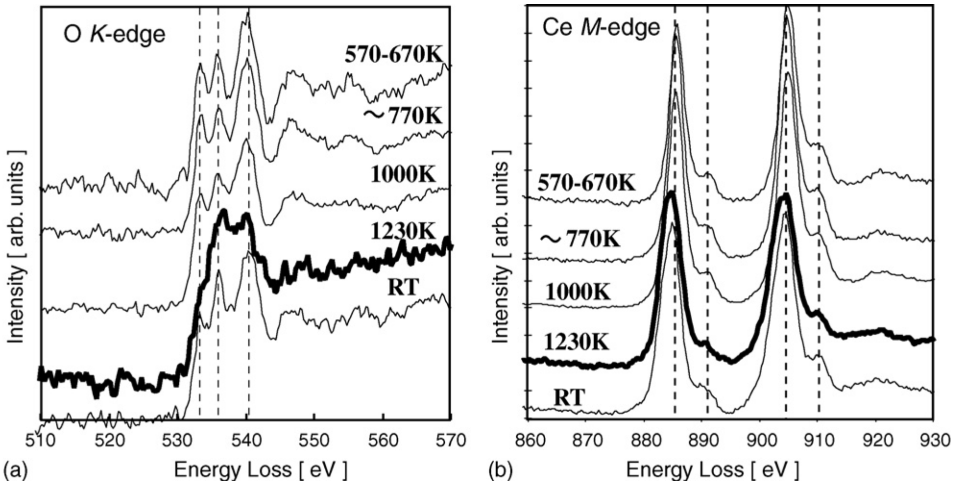

Fig. 2. EELS spectra of O-K edge (a) and Ce-M edge (b) of CeO_2 corresponding to the TEM images shown in Fig. 1 during heating.

The apparent reduction of CeO_2 is observed in the O-K edge spectrum at 1230 K, while the reduction state was reported at around 873 K under hydrogen atmosphere [13]. In Fig. 2a, the spectrum at 570–670 K shows three major peaks at 531, 534 and 538 eV. The intensity of the peak at 531 eV decreases by heating, and is greatly reduced at 1230 K, which means the reduction from Ce^{4+} to Ce^{3+} [9]. The reduced CeO_2 absorbs residual water or oxygen and is oxidized in the electron microscope during the cooling process from 1230 K to room temperature since the peak at 531 eV recovers again in the O-K edge EELS spectra. The vacuum condition of the electron microscope is approximately $3–5 \times 10^{-5}$ Pa and the residual water or oxygen is enough for this recovery, because the equilibrium oxygen pressure of Ce_2O_3 is estimated as 1.3×10^{-53} Pa at 298 K [14].

The reduction and oxidation of CeO_2 are also seen in the Ce-M edge EELS spectra in Fig. 2b. The two major peaks called white lines are observed. By elevating the temperature, the intensity ratio of the two peaks changes, and the positions of the peaks also slightly shift to the lower energy region. These changes are attributed to the presence of the change from Ce^{4+} to Ce^{3+} [12,15]. From the spectrum at 1230 K, there seem to co-exist the two oxidation states of Ce^{3+} and Ce^{4+}. In the spectrum at room temperature, the peak ratio and positions almost recover to the original state.

The reduction similar to Fig. 2 was observed in our previous experiments [9] at room temperature (without heating) under higher or longer-time electron-beam irradiation. The effects of the electron irradiation are, first, direct damage formation such as oxygen vacancy formation in CeO_2 by electron stimulated desorption (ESD) or direct knock-on, and second, direct or indirect heating of a sample via electron or ionic excitation. In our previous experiments, the first effect seems to be serious, because high density of ordered oxygen vacancies was observed, and the reduction observed by EELS seems to be associated with the oxygen vacancies. In the present experiment, our aim is to reduce the first effect of the irradiation as far as is possible, and to examine the thermal effect purely. Of course, it is not possible to prevent the irradiation damage completely, and the observed reduction at 1230 K may be caused by both effects.

Fig. 3 shows the successive series of HRTEM images of Au particles on a CeO_2 support during heating from room temperature to 910 K. The small Au particle indicated by an arrow in Fig. 3c disappears at 870 K as shown in Fig. 3d. Small Au particles under 5 nm in diameter almost disappear at 910 K, and only large Au particles remain. There is no migration of Au particles during the present disintegration and growth process. This means that Au particles grow by Ostwald ripening process accompanied by transport of Au atoms by surface diffusion. It is also confirmed that the Au particles have crystalline structure during heating since the Au(1 1 1) lattice fringes are observed. It is known that the melting point of small particles decreases depending on the size of particles [16], but the melting is not observed for the Au particles on CeO_2 in the present in situ heating experiment. Fig. 4 shows the change of diameter of each Au particle indicated in Fig. 3a in the heating process. Although the apparent change of diameter is not observed until 800 K, the Au particles start to grow at over 800 K. The small particles (particle 3 and 4) also grow at 870 K, and they disappear around 900 K.

Fig. 5 shows successive HRTEM images during the observation at 1000 K. The images were created from the movie recorded by a video tape recorder through a TV camera. On the CeO_2(1 1 1) surface with atomic steps, there remains a small Au particle, where the epitaxial orientation relationship of CeO_2(1 1 1)//Au(1 1 1) is clear. It is successfully observed that the Au particle is disappearing layer by layer during the observation. The monolayer Au is observed in the later stage of the process as indicated by an arrow in Fig. 5e. The present real-time structure change is rather similar to those observed under the electron beam irradiation at room temperature in our previous experiments [8,9], although the speed of the present shape change is much higher due to the high temperature. The present atomic-scale change seems to reveal the atomic process of surface diffusion, although there is another possibility of the sublimation process of Au. This is because the temperature programmed desorption (TPD) study indicated that the

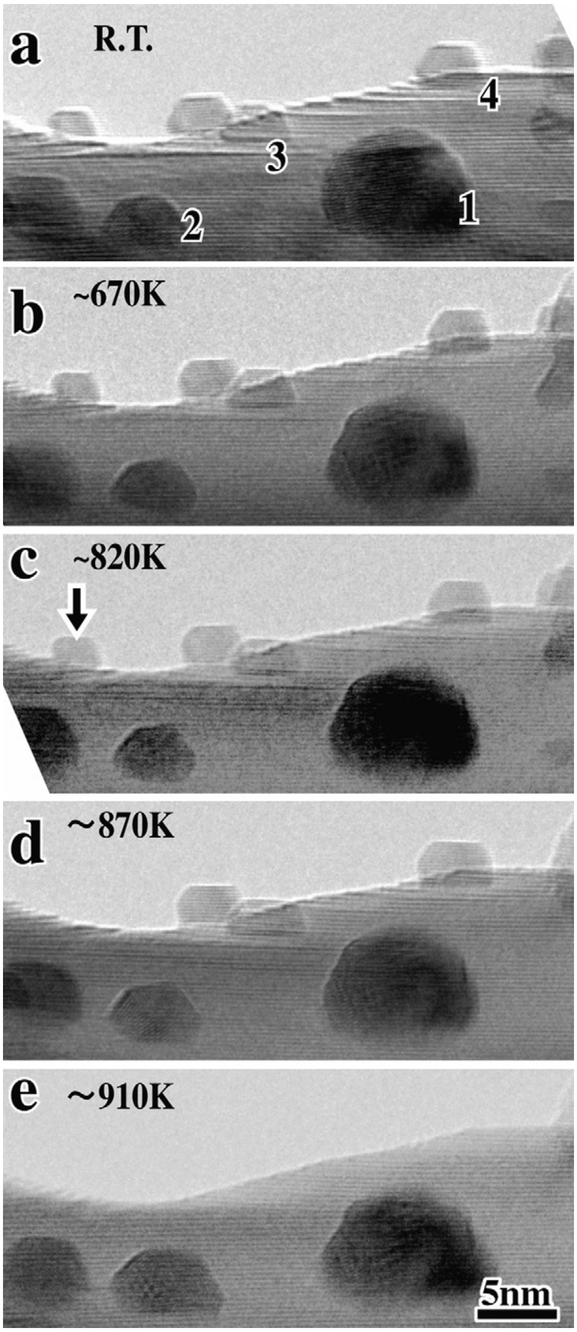

Fig. 3. HRTEM images of Au particles on CeO_2 during heating at: room temperature (a), 670 K (b), 820 K (c), 870 K (d), and 910 K (e).

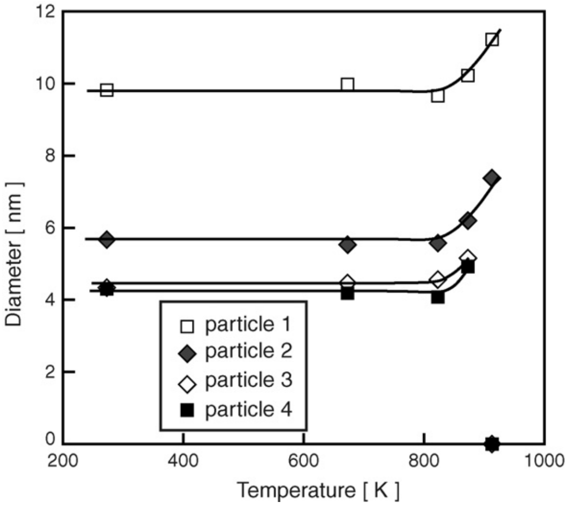

Fig. 4. Variation of the size of each Au particle in the heating process in Fig. 3.

sublimation started around 1000–1100 K depending on the kind of metal oxide supports [17,18]. In situ TEM observation of a Ag particle on graphite during heating is reported by Lee et al. [19], and they show that the height to width ratio of a Ag particle is constant during the disintegration process at 950 K. The height to width ratio of Au on CeO_2 is decreasing with the size of a Au particle in our experiment, because of the small change of the interface contact area similar to the previous observations [8,9]. The smaller value of height to width ratio means larger adhesion energy between Au and CeO_2 [20]. The melting of Au is not observed even for the present Au monolayer. It is suggested that the Au particle is strongly bonded to the CeO_2 surface with some anchoring features, thus the melting of Au particles are not observed during the heating at 1000 K.

Iridium particles on CeO_2 at elevated temperature were also observed for comparison with Au particles. Iridium particles on CeO_2 are initially oxidized by heating in the air during preparation process [21]. Iridium oxides are easily reduced by heating at over 473 K in a specimen chamber of the electron microscope. Fig. 6 shows the TEM images of Ir particles supported on CeO_2 at 950 K. During the observation, two Ir particles indicated by arrows in Fig. 6a migrated to each other, and coalesced immediately with in 0.4 s as shown in Fig. 6b. The coalesced Ir particle migrates on the CeO_2 surface again for several seconds. The moiré fringes are observed in the Ir particles, which means that the Ir particles migrate with keeping the crystalline structure without melting. This is rather natural because of high melting temperature of Ir (2683 K). In the observation of the heating process, the Ir particles hardly grow in the temperature range from 673 to 1000 K. The apparent growth is observed after the CeO_2 supports start to change the surface shape at the temperature over 1000 K. Smoothed surface shapes of CeO_2 should be beneficial for the Ir particle migration. It is clear that the growth process of Ir particles is quite different from that of Au particles. The migration of Au particles was seldom observed in Fig. 3.

Fig. 7 shows schematic drawing of the growth processes of Au and Ir particles on CeO_2 at high temperature. The Au particles grow by Ostwald ripening process by transport of atoms. The surface diffusion seems to be dominant at around 800 K as observed in Figs. 3 and 4. It also seems that the atomic diffusion of Au is rather easy on CeO_2 even at room temperature, although the oxidation state or density of oxygen vacancies in CeO_2 seem to have significant effects on the Au diffusion [8,9]. The Au particles themselves do not migrate on the CeO_2 surface. This is because the strong interfacial adhesion, which should be caused by the easy formation of coherent and off-stoichiometric interfaces [22,23]. On the other hand, the atomic diffusion is not so easy for Ir at least for the

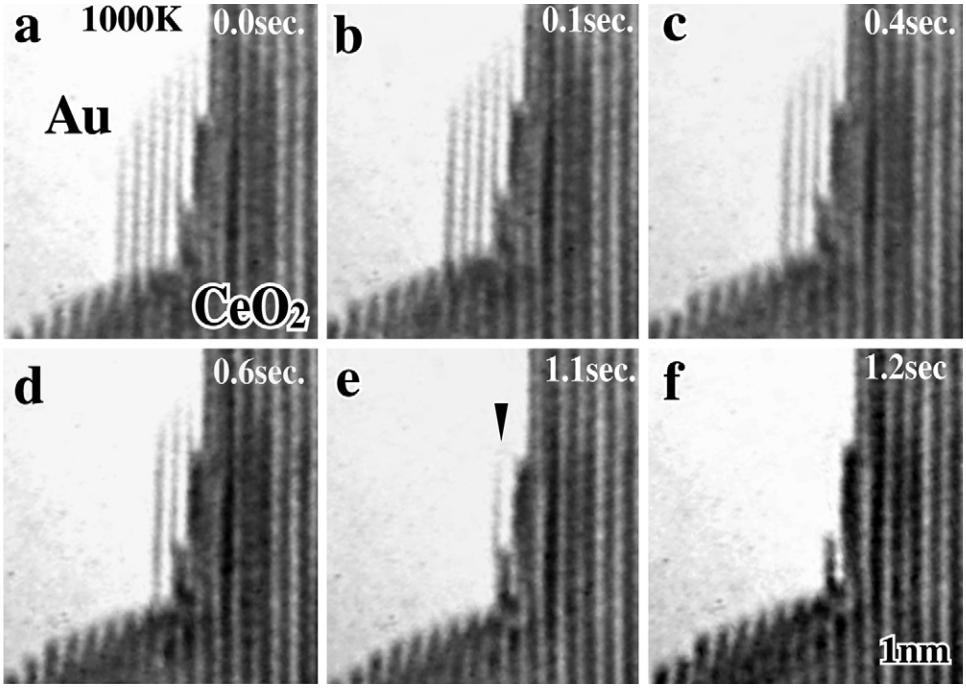

Fig. 5. Successive HRTEM images during the observation at 1000 K.

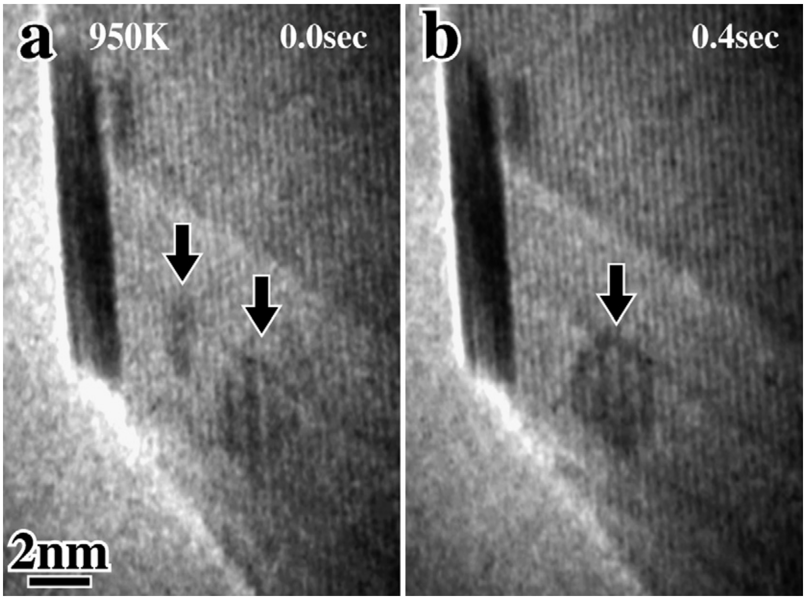

Fig. 6. TEM images of Ir particles on CeO_2 during heating at 950 K. Coalescence process of Ir particles before (a) and after (b) was observed.

examined temperature range less than 1000 K, which is consistent with a rather high melting point of Ir. Thus, the growth of Ir particles occurs through the migration of Ir particles itself at the high temperature over 1000 K, where the CeO_2 surface can become smooth and the particles can get enough thermal kinetic energies. Of course, the Ir/CeO_2 interface itself does not seem to have strong adhesion with special exitaxial relationship.

From the present results, it is clear that the diffusion of Au and the strong interface adhesion are key factors of the novel structure changes of Au particles on CeO_2. And both factors are seriously affected by the oxidation state or density of oxygen

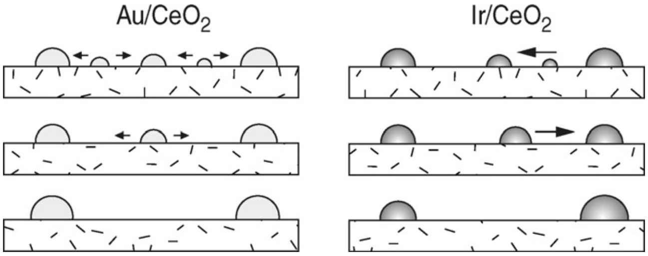

Fig. 7. A schematic drawing of growth processes of Au and Ir particles on CeO_2.

vacancies in the CeO_2 surface or bulk CeO_2. In the present results, it has been shown that the temperature as well as electron beam irradiation has serious effects on the structure change of Au particles on CeO_2 through the enhancement of Au diffusion caused by the formation of oxygen vacancies in the CeO_2 surface or bulk CeO_2 and the thermal energy of Au atoms. The detailed effects of the surface or bulk state of CeO_2 on the Au diffusion are not clear at present, which will be studies in the near future through the experiments of controlling the atmosphere, for example.

4. Conclusion

The following conclusions have been drawn through analytical TEM observations of Au particles supported on CeO_2 during heating in the electron microscope.

(1) The structure changes of Au particles on CeO_2 supports in the heating process was successfully observed by using a specimen heating holder.
(2) The disintegration process of Au particles was successfully observed in the atomic scale, where Au particles have crystalline structure during shrinking until an atomic layer.
(3) In situ TEM observation of the growth process of Au particles on CeO_2 by heating revealed that the Ostwald ripening is a dominant process.
(4) By similar in situ TEM observation, it was revealed that the migration of Ir particles on CeO_2 surfaces is a dominant growth process at high temperature over 1000 K.

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