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Molecular dynamics simulation for ultrafine gold particles deposited on metal oxides

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Abstract

In this review we summarize the results of the molecular dynamics simulations performed by our recently developed code on the simulation of the formation process of metal-oxide supported ultrafine metal particles. First we present our investigations on the formation processes of ultrafine gold particles on the metal-oxide surface. We also show the effect of substrate temperature and deposition rate of the Au particles on the generated gold clusters. Furthermore, we investigate the influence of different kinds of surface defects on the formation process of supported Au clusters and the role of these effects in the production and design of highly dispersed ultrafine Au particles.

Keywords: Molecular dynamics; Ultrafine gold particles; Formation process; Sintering process; Metal oxide surface; Defects

1. Introduction

Ultrafine metal particles have attracted larger and larger attention due to their high activities in heterogeneous catalytic processes [1,2]. Moreover, they are also important in the design of electronic, magnetic or optical devices and other advanced materials. Among them the noteworthy performance of ultrafine gold particles, especially metal-oxide supported gold particles has recently been exposed in the low temperature oxidation of carbon-monoxide, in the partial oxidation of different hydrocarbons, and in other important catalytic reactions (see, e.g., Refs. [3–21]). In these processes both the shape and size of the gold particles, and the support have an important role in the genesis of catalytic activity. In order to describe this role a large number of experimental work have been done using different techniques such as MBE, SEM, HRTEM, RHEED, LEED, etc. [22–26].

In the past decades theoretical modelling of the catalytic systems has become the most promising tool for understanding and explaining the experimentally measured results and to predict new features [27–29]. Computer-assisted material design is a new area of chemistry which has been brought about by the significant advance in computer technology and theoretical chemistry of the last years, such as quantum chemistry (QC), molecular dynamics (MD), molecular mechanics (MM) or the different Monte Carlo (MC) applications, together with computer graphics (CG) methods [27–29]. Since MD methods have proved to be effective in describing different chemical systems such as

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zeolites, metallosilicates, or superconductor films (see, e.g., Refs. [30–35]), this methodology seemed to be excellent in modelling ultrafine metal particle-support systems. Using MD approach we could succesfully explain: (i) formation processes of the supported gold clusters [36–40], (ii) interaction between gold clusters and the metal-oxide surface [39], (iii) influence of the surface defects upon structure of the gold particles at different temperatures [38,40], (iv) sintering processes of supported gold clusters [36,40], and (v) the role of the point defects in the production of ultrafine gold clusters [38,40]. In the present paper we review the most important results in order to give an overall picture about the formation and sintering processes, the fine structure and the dynamic behaviour of the supported ultrafine gold particles. We also present how the theoretical simulation can be utilized in the design of highly dispersed ultrafine gold particles.

2. Development of a new MD code for simulation of deposition process of ultrafine metal particles on metal-oxides

Our theoretical investigations were carried out by means of molecular dynamics which is an ultimate tool for simulating molecular-scale models of matter [41]. The calculations were performed using the program developed in our laboratory [37] on the basis of the MXDORTO code [42], which enabled us to study the formation processes of the ultrafine metal particles on substrate surfaces. This modification involves a novel model system in which the randomly deposited atoms are generated in a special source as well as the deposition rates, the distance of the source from the surface, the time interval between the deposited Au atoms and the temperature of the surface are variable parameters.

The atomic motion were calculated by the Verlet algorithm [43], while the electrostatic interactions were computed by the Ewald method [44]. The temperatures were controlled by scaling the atomic velocities. The form of the two-body, central force interatomic potential used in the calculations is the following:

$$\begin{aligned}u(r_{ij}) = {} & Z_iZ_je^2/r_{ij} + f_0(b_i+b_j)\\ & \times\exp\left[(a_i+a_j-r_{ij})/(b_i+b_j)\right]\\ & + D_{ij}\left\{\exp\left[-2\beta_{ij}(r_{ij}-r_{ij}^*)\right]\right.\\ & \left.-2\exp\left[-\beta_{ij}(r_{ij}-r_{ij}^*)\right]\right\}.\end{aligned}$$

Here the first, second and third terms refer to the Coulomb, exchange repulsion and Morse interactions, respectively. Z_i is the atomic charge, e is the elementary electric charge, r_{ij} is the interatomic distance, and f_0 is a constant. The parameters a and b represent the size and the stiffness, respectively, in the exchange repulsion interaction, while D_{ij}, r_{ij}^* and β_{ij} represent the bond energy, the bond equilibrium distance and the stiffness, respectively, in the Morse function. The parameters of this equation were determined to reproduce the structures of various metal-oxides and metal-crystals. Particularly the Morse terms for the Au–metal oxide interactions were chosen so as to reproduce the experimental results for supported Au particles [37,39].

We chose MgO(100) surface as an appropriate support because MgO can be used inter alia as support for model catalysts (e.g., Refs. [45–48]). The calculations were performed on HP 710 and 712/60 workstations. For the static visualization we used an SGI Indigo 2 workstation and the BIOSYM Insight II program package [49]. For the dynamic visualization the MOMOVIE and RYUGA codes [50] developed in our laboratory were employed.

3. Deposition processes [37,38]

The dynamic process of the Au atoms in the formation of Au clusters on the MgO(100) plane was simulated by MD and CG. Fig. 1 shows the formation process of an Au cluster on a MgO(100) plane at 300 K, when 20 Au atoms

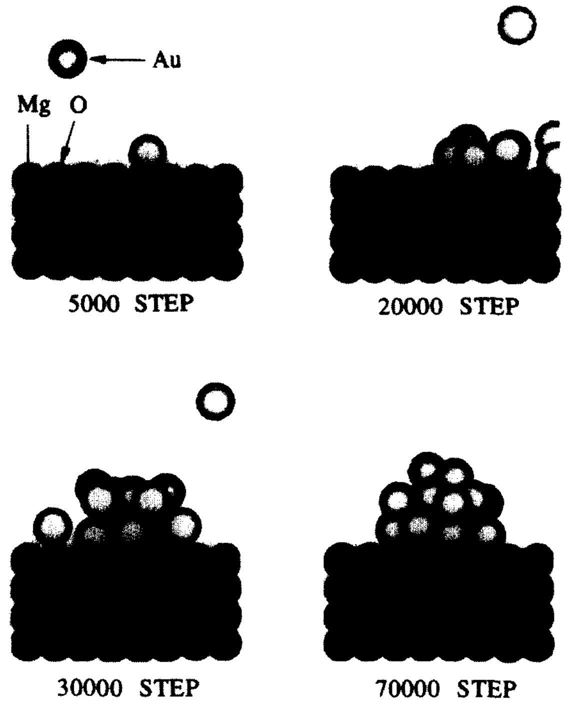


Fig. 1. The formation process of ultrafine Au particles on MgO(100) plane at 300 K.

with a deposition rate of 180 m/s were deposited one by one after every 2000 time steps. When any Au atom approached the MgO(100) plane, initially it migrated on the surface with high mobility. After the Au atoms aggregated gradually, finally a hemispherical Au cluster was formed on the MgO(100) plane. The shape of the Au cluster was quite similar to that obtained experimentally [25]. These results validated the applicability of our new MD code for the atomistic understanding of the deposition processes of ultrafine metal particles on substrate surfaces which cannot be derived from experimental studies.

In relation to the metal deposition by evaporation, sputtering or molecular beam epitaxy, the effect of the deposition rates of metal atoms or the effect of temperature of metal oxide substrates on the ultrafine metal particle formation over substrate surfaces are interesting phenomena. MD simulations with various deposition velocities of Au atoms were performed at 300 K as well as simulation with various temperatures of the MgO substrate, using constant (180 m/s) deposition rate.

3.1. Effect of the deposition rate

Since the deposition rate of Au atoms in the above simulation studies was very slow, namely 180 m/s, the deposition process of 20 Au atoms with a deposition rate of 1080 m/s on the MgO(100) plane was simulated. All of the Au atoms were repelled by the MgO(100) plane and no Au atoms were fixed on the surface. Fig. 2a–c represent the final shapes of the Au clusters on MgO(100) plane, when 20 Au atoms were deposited with the deposition rates of 720, 540 and 180 m/s, respectively. When the deposition rate was 720 m/s (Fig. 2a), 4 Au atoms were fixed on the MgO(100) plane and the other Au atoms were repelled from the surface. When the deposition rates of the Au atoms were 540 m/s (Fig. 2b) and 180 m/s (Fig. 2c), 10 and 19 atoms were fixed on the surface, respectively. It

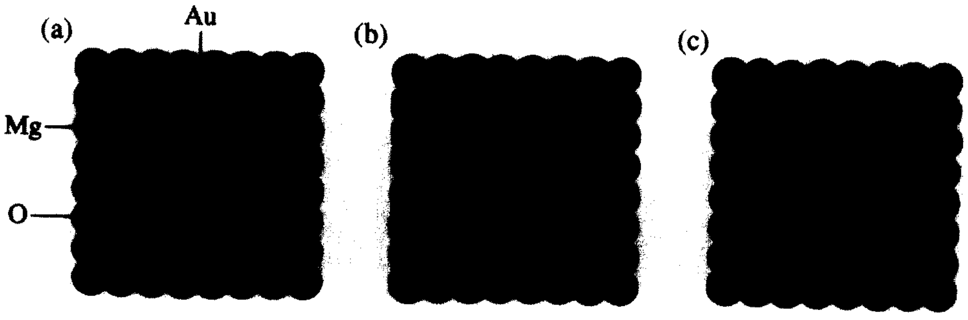


Fig. 2. The final shapes of the Au clusters formed on MgO(100) at 300 K. The deposition rates of Au atoms are: (a) 720 m/s, (b) 540 m/s, and (c) 180 m/s.

was found that the slower deposition rates of Au atoms lead to a larger number of Au atoms fixed on the MgO(100) plane.

3.2. *Effect of substrate temperature*

MD calculations were also carried out at 1000 K. As the result of this simulation, a hemispherical Au_{15} cluster was formed on the smooth MgO(100) plane, while 5 atoms from the initial 20 atoms were repelled from the surface during the simulation. When the temperature was 300 K, an Au_{19} cluster was formed on the smooth MgO(100) plane. Although one Au atom was repelled from the surface, almost all Au atoms, i.e., 19, could be fixed on the MgO(100) plane. It was found that more Au atoms were fixed on the MgO(100) plane at lower temperatures. It is observed from the dynamic visualization that the hard collision between Au atoms and MgO surface, just after the Au atom approached the surface, led to the repulsion of deposited Au atoms. The deposition rates of the Au atoms were the same at both low (300 K) and high (1000 K) temperatures, however more Au atoms were repelled from the MgO surface at higher temperatures. This phenomenon could be understood from the higher vibrational mobility of the Mg^{2+}- and O^{2-}-ions in the MgO(100) plane at higher temperature. Hence, as the temperature is increased, the collision force is enhanced and the repulsion of Au atoms becomes more frequent.

Although the number of Au atoms fixed on the MgO(100) plane cannot be discussed quantitatively from the above-mentioned results, it is clearly indicated, that lower temperature of the MgO substrate and lower deposition rates of the Au atoms are effective to fix more Au atoms efficiently on the MgO(100) plane.

4. Surface defects [37,38]

It has been shown experimentally that surface defects, such as grooves, steps, kinks and va-

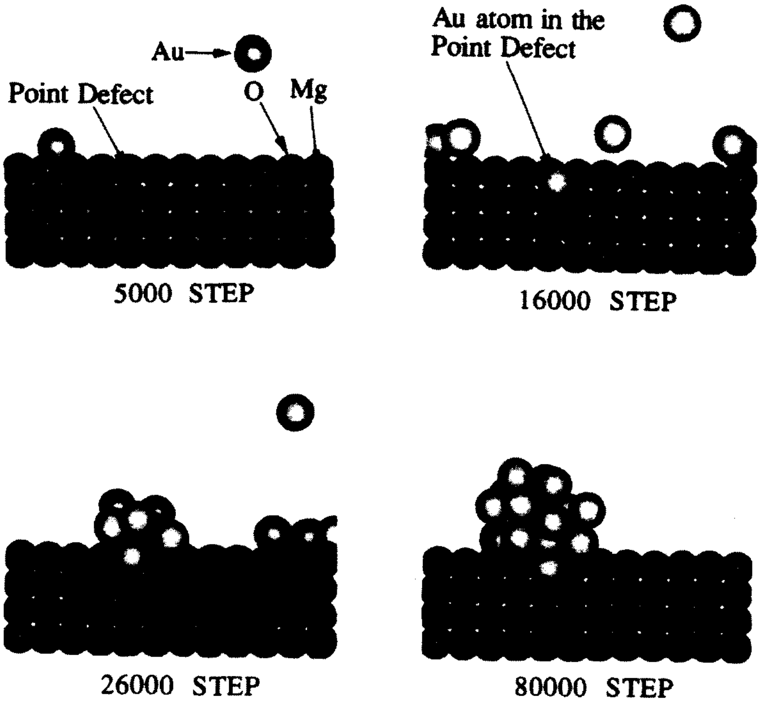


Fig. 3. The formation process of ultrafine Au particles on MgO(100) with a point defect at 300 K.

cancies greatly affect the structure of metal clusters on substrate surfaces (see, e.g., Refs. [22–24,51,52]). MD simulations were performed to understand the effect of defects in the MgO(100) plane on atomic scale.

Fig. 3 shows the formation process of an Au cluster on the MgO(100) plane with a point defect at 300 K during 80 000 time steps. It was found that a hemispherical Au cluster was formed just over the point defect in the MgO(100) plane. In order to investigate the formation mechanism attention was given to the dynamics and behaviour of each Au atom during the formation process. It was observed that an Au atom was trapped in a point defect on the MgO(100) plane at the 16 000th time step as shown in Fig. 3. After other Au atoms came in contact with the trapped Au atom in the point defect, a gradual formation of the Au cluster occurred over the point defect. Finally, a hemispherical Au cluster was formed just over the point defect in the MgO(100) plane. Hence, the Au atom trapped in the point defect has a role of a nucleation center for the Au cluster formation on the MgO(100) plane at 300 K. Moreover, this is the reason why the Au cluster was formed just over the point defect in the MgO(100) plane.

Fig. 4 shows the formation process of an Au cluster on the MgO(100) plane with a point defect at 1000 K during 80 000 time steps. In this simulation we could observe that a Au cluster was formed on an unspecified site on the MgO(100) plane which is markedly different from the result of the simulation at 300 K. Analysing the formation mechanism at 1000 K we found the followings. After an Au atom was trapped in the point defect at the 20 000th time step, it was released from the point defect at the 28 000th time step. Moreover another Au atom was trapped in the point defect at the 36 000th time step again, however it was also released

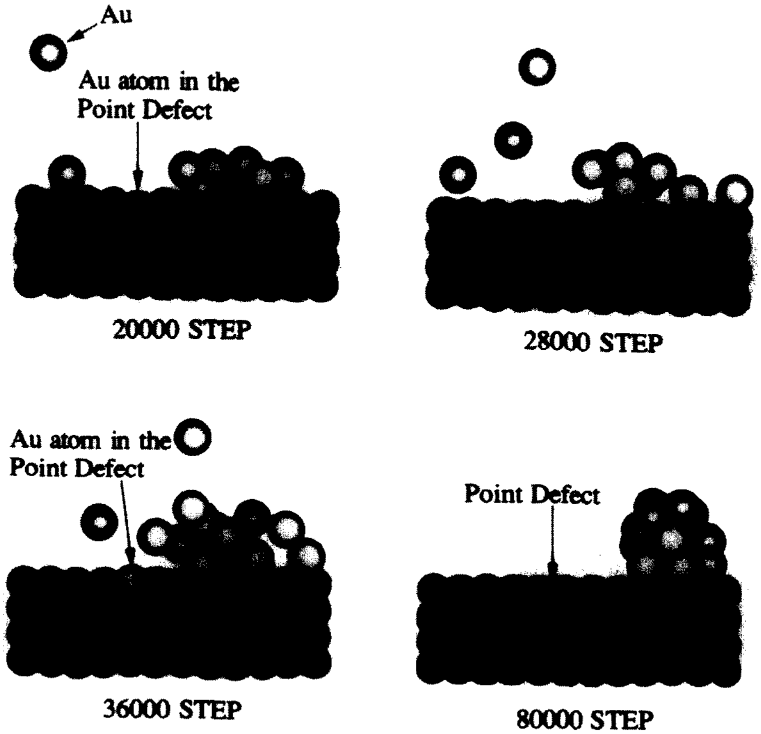


Fig. 4. The formation process of ultrafine Au particles on MgO(100) with a point defect at 1000 K.

from the point defect at the 40 000th time step. The higher vibrational mobility of Mg^{2+}- and O^{2-}-ions adjacent to the defect at higher temperatures was one of the reasons for the frequent release of the trapped Au atom, in addition to the higher translational mobility of the Au atoms. Finally, an Au cluster was formed in an unspecified site on the MgO(100) plane. This is due to the easy release of the Au atoms trapped in the point defect and the smaller probability of nucleation center formation in the point defect at higher temperature. In other words, the higher mobility, which is a consequence of the higher temperature, led to the random location for the ultrafine Au particles on the MgO(100) plane with a point defect.

The results of the simulation with a point defect on the MgO(100) surface indicate that modification of the surface is effective to reduce the mobility of the Au clusters and, hence, stabilize the ultrafine gold particles on the metal-oxide surface, especially at lower temperature.

5. Design of highly dispersed ultrafine gold particles [40]

5.1. Utilization of two point defects

Ultrafine dispersion of metals on supports is desired for achieving maximum catalytic performance, since the higher surface area of metals often leads to higher turn-over frequencies [9]. In order to stabilize small Au clusters on metal-oxide surface we investigated the dynamic behaviour of the gold particles on MgO(100) plane with different surface properties.

Fig. 5 shows the formation process of Au clusters on the MgO(100) plane with two point defects at 300 K. Here both point defects were composed of single Mg^{2+}- and O^{2-}-vacancies, and they are separated by 22.68 Å. The formation of two Au clusters just over the point defects was observed on the MgO(100) plane as shown in the CG picture at the 100 000th time step, which is in remarkable contrast to that on

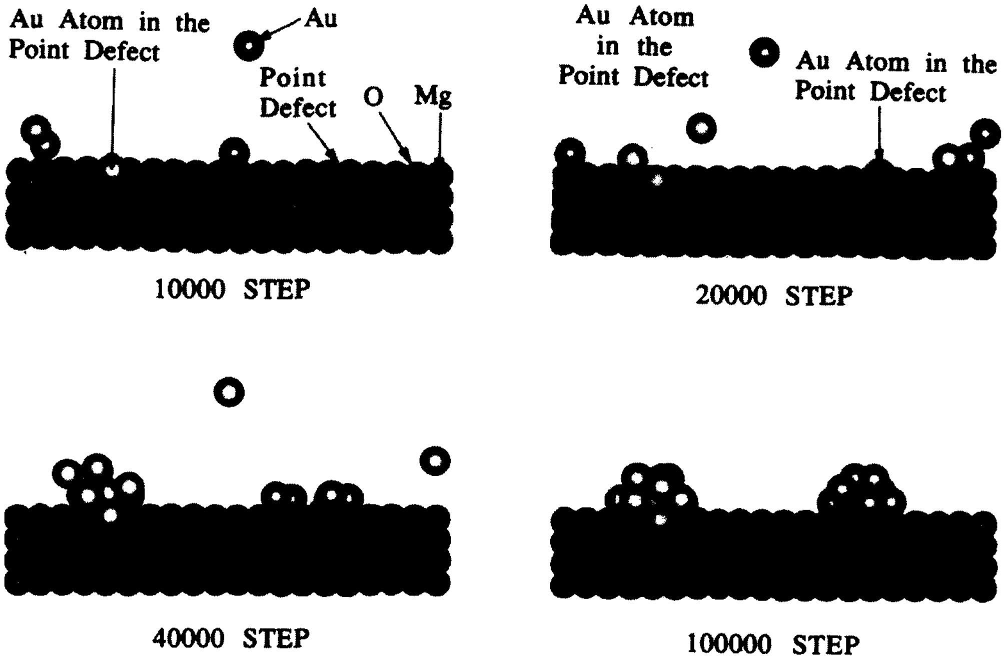


Fig. 5. The formation process of ultrafine Au particles on MgO(100) with two point defects at 300 K.

the smooth MgO(100) plane. In the latter case only a single gold cluster was formed. This phenomenon is due to the fact that a trapped Au atom in each point defect played a role of the nucleation center. These results suggested that an increase in the amount of the point defects leads to a larger number of nucleation centers and the realization of ultrafine dispersion of Au particles on the MgO(100) plane. It was also found that the point defects substantially reduced the mobility of the gold clusters which means that the point defects are also effective for preventing the sintering of the gold particles on the surface.

Analysing the effect of temperature on the dynamic behaviour of the two gold clusters formed over the point defects of the MgO(100) plane we found that at higher temperatures, e.g., 700 K the shapes of the two Au clusters were gradually deformed and finally they became aggregated to form a single large Au cluster on the surface, as shown in Fig. 6. It is obvious from these findings that the mobility of the Au atoms and clusters is raised and the sintering of the Au clusters is promoted by the increment of temperature. Hence, high temperatures counteract the performance of point defects in the ultrafine dispersion of Au clusters on the MgO(100) plane.

5.2. *Succesful design of highly dispersed ultrafine metal particles in wider temperature region*

Based on these experiences, a novel sophisticated technique was suggested to realize stable ultrafine gold dispersion on MgO(100) surface both at low and high temperatures. An MgO(100) plane with two monoatomic steps was proved to be effective support for highly dispersed ultrafine gold particles. It was clarified that the monoatomic step plays the same role as the point defect during the formation of a single Au cluster on MgO(100) plane [38].

Fig. 7 shows the formation process of Au clusters on the MgO(100) plane with two monoatomic steps at 300 K. Here the monoatomic steps are separated by a distance of 25.27 Å. An Au atom was trapped in the right step at the 10 000th time step, and another Au atom was trapped in the left step at the 20 000th

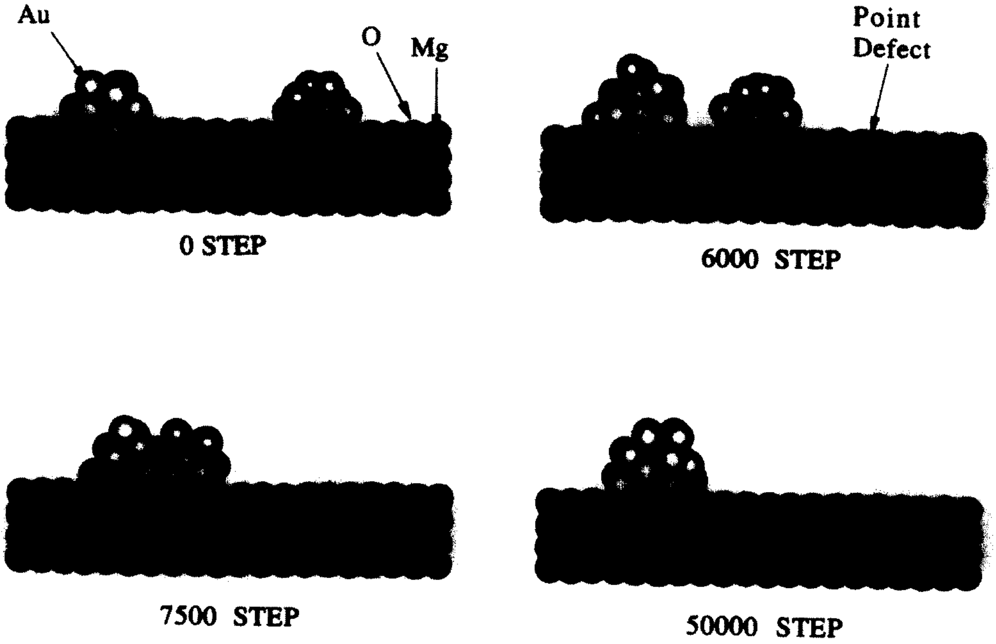
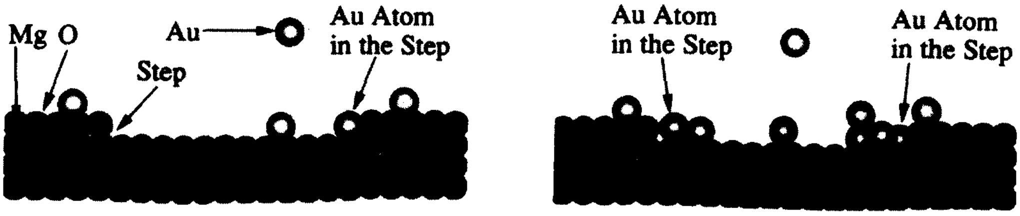


Fig. 6. The dynamic behaviour of ultrafine Au particles on MgO(100) with two point defects at 700 K.

time step. After other Au atoms came in contact with both trapped Au atoms, finally two hemispherical Au clusters were formed just over the two surface steps on the MgO(100) plane. Thus, the artificial construction of surface steps appeared also to be effective for realizing the ultrafine dispersion of Au particles on the MgO(100) plane.

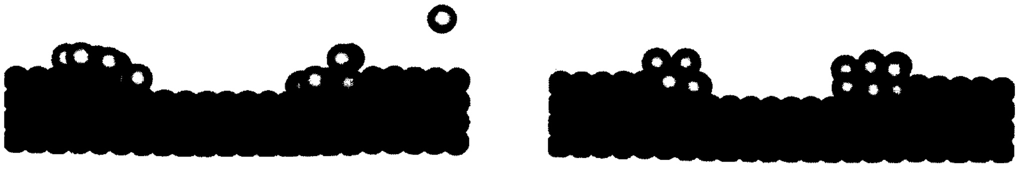
The stability and mobility of two ultrafine Au particles just over the monoatomic steps in the MgO(100) plane at high temperatures were also investigated. The shapes of two Au clusters were maintained and the aggregation did not take place aven at 700 K, which was significantly different from that observed for the MgO(100) plane with two point defects. In the latter case each Au cluster over the point defect was fixed by the single Au atom trapped in the point defect. Hence, once the trapped Au atom was released from the point defect, the Au cluster gained high mobility and transferred to another Au cluster. On the other hand, the Au cluster over the monoatomic step was fixed by many Au atoms trapped in the step. Since the release of all trapped Au atoms in the surface step is energetically hindered, the aggregation of Au clusters on the surface steps is hardly to take place. This result suggests that the surface steps are more effective to maintain the high dispersion of Au particles on the MgO(100) plane than the point defects.

These results can be utilized in the catalyst research because most catalysts reach high performance at higher temperature, such as 600–1000 K. Hence, it is essential to develop stable catalysts which do not undergo significant deactivation even at high temperatures for practical application of supported metal catalysts. The aggregation of metal clusters on metal-oxide substrates (sintering processes) provides one of the common reasons for the deactivation of supported metal catalysts, such as Pt, Pd, etc., in general and especially the ultrafine Au particles. In some studies [36] it was clarified that Au clusters are readily aggregated on a smooth MgO(100) plane even at 300 K. The abovementioned results suggest that the surface modification on the MgO(100) plane is effective to reduce the mobility of Au clusters, and hence to avoid the aggregation and sintering of ultrafine Au particles on the MgO(100) plane. Therefore, we hope that our results can be used in the design of novel, more stable and effective catalysts.



10000 STEP

20000 STEP



35000 STEP

60000 STEP

Fig. 7. The formation process of ultrafine Au particles on MgO(100) with two monoatomic steps at 300 K.

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