Oxygen-induced morphological changes of Ag nanoclusters supported on TiO$_2$(110)

Xiaofeng Lai, Todd P. St.Clair and D. Wayne Goodman*

Department of Chemistry, Texas A&M University, P.O. Box 30012, College Station, TX 77842-3012, USA

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The effect of in situ O$_2$ exposure on TiO$_2$(110)-supported Ag nanoclusters was investigated using X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM). An oxygen-induced cluster ripening was observed by STM after Ag/TiO$_2$(110) was exposed to 10.00 Torr O$_2$ for 2 h in an elevated-pressure reactor. The Ag clusters exhibit a clear bimodal size distribution after O$_2$ exposure due to Ostwald ripening: some clusters increase in size while other clusters decrease in size. The cluster density also increased 5–15% after O$_2$ exposure, indicating redispersion simultaneously occurs with ripening. It is shown that intercluster transport is likely accomplished through the formation of Ag$_2$O.

1. Introduction

A primary goal of heterogeneous catalysis is to elucidate the relationship between catalyst structure and activity. However, the achievement of this objective is often complicated by the morphological and structural changes that surfaces sometimes undergo at reaction pressures. These adsorbate-induced surface restructurings result from the reorganization of surface atoms near the adsorption site of a chemisorbed atom or molecule. Depending on the strength of the surface–adsorbate bond, the surface may experience different degrees of restructuring, from weak local relaxation to massive transportation of surface atoms. In the case of “real world” catalysts, which often consist of small metal particles supported on oxide substrates, one is not only concerned with changes associated with the substrate surface, but the supported metal clusters as well. Metal nanoclusters contain a relatively small number of atoms, thus the surface atoms can be easily influenced because of their low coordination number, making supported nanoclusters vulnerable to adsorbate-induced morphological changes. If this restructuring of metal clusters results in cluster growth, then active metal surface area has been lost and the catalyst may become deactivated.

The physical and chemical properties of supported metal clusters, and the interactions between these clusters and different substrates, have been widely investigated. The scanning tunneling microscope (STM) is particularly suited for studying such interactions because it can directly probe cluster morphology and structure. For example, STM results indicate that exposure of CO pressures between $10^{-3}$ and $10^{-1}$ mbar to Rh/TiO$_2$(110) – $(1 \times 2)$ led to a significant agglomeration of Rh clusters. This phenomenon was attributed to the formation of Rh–CO bonds (185 kJ mol$^{-1}$) that promote disruption of the weaker Rh–Rh bonds (44.5 kJ mol$^{-1}$). Similar effects have also been observed for Ir/TiO$_2$(110) – $(1 \times 2)$. In a recent study of CO oxidation over model Au catalysts, the well-known structure sensitivity and the stability of Au nanoclusters to CO and O$_2$ were investigated. STM in conjunction with

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reaction kinetics measurements revealed that the structure sensitivity was related to a quantum size effect with respect to the thickness of the Au islands: maximum reactivity was observed for Au clusters with diameters of \( \approx 3.5 \) nm and heights less than 3 atomic layers. It was observed in the course of these CO oxidation experiments that \( O_2 \) exposure resulted in sintering of the Au nanoclusters. Fig. 1 shows two STM images of 0.25 monolayer (ML) Au/TiO\(_2\)(110) before (top image) and after (bottom image) exposure to 10.00 Torr \( O_2 \) for 2 h. The effect of the \( O_2 \) exposure was a decrease in cluster density (number of clusters per unit area) and an increase in cluster size, from 2.6 nm \( \times \) 0.7 nm (diameter \( \times \) height) to 3.6 nm \( \times \) 1.4 nm. These results demonstrate the utility of STM for studying supported metal nanoclusters by establishing a correlation between the structural, electronic and reactivity properties of model Au catalysts. Furthermore, given the sintering effect of \( O_2 \) on Au nanoclusters, it is expected that other metal nanocluster systems could also be susceptible to \( O_2 \)-induced morphological changes.

Silver is a metal whose interaction with \( O_2 \) environments is of interest primarily because of its use as an industrial catalyst for two important oxidation reactions: ethylene oxidation to ethylene

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**Fig. 1** STM images of Au clusters on TiO\(_2\)(110) \(- (1 \times 1)\) (2.0 V, 2.0 nA). The dosing flux is 0.083 ML min\(^{-1}\) and the Au coverage is 0.25 ML. Top: Fresh Au/TiO\(_2\)(110) deposited at room temperature and then annealed to 600 K. Bottom: 0.25 ML Au/TiO\(_2\)(110) exposed to 10.00 Torr \( O_2 \) for 2 h at 300 K. The \( O_2 \) exposure results in decreased cluster density and increased cluster size.
epoxide and methanol oxidation to formaldehyde. To gain additional insight into the role that O$_2$ plays in cluster growth, Ag clusters deposited on a TiO$_2$(110) surface were characterized using XPS and STM before and after O$_2$ exposures.

2. Experimental

Experimental details have been published elsewhere. Briefly, the experiments were performed in a combined elevated pressure reactor-UHV system with a base pressure of 5 \times 10^{-11} Torr. The system is equipped with a double pass cylindrical mirror analyzer (CMA) for Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS), reverse view low energy electron diffraction (LEED) optics, and an Omicron UHV-STM. A TiO$_2$(110) single crystal (Commercial Crystal Laboratories, Inc.), typically prepared by cycles of Ar ion bombardment and vacuum annealing to 1100 K, was found to be sufficiently clean, flat, and conductive for electron spectroscopies and STM studies. Ag clusters were evaporated onto the TiO$_2$(110) surface from a source containing high purity Ag wire wrapped around a Ta filament that could be heated resistively. The Ag doser was extensively outgassed prior to use. The experimental Ag flux of 0.125 ML min$^{-1}$ was calibrated with a Re(0001) substrate using AES and STM. One ML Ag coverage corresponds to $1.39 \times 10^{14}$ atoms cm$^{-2}$.

A combined elevated pressure reactor-UHV system was used for studies of high-pressure gas exposures and reactions. Following preparation and characterization in the primary UHV chamber, the sample was transferred in situ into the elevated-pressure reactor through double-stage differentially pumped Teflon sliding seals. This pumping arrangement provides a convenient way of performing elevated-pressure adsorption and reaction kinetics studies in the range of $1 \times 10^{-10}$ to $1 \times 10^3$ Torr, while maintaining UHV pressures in the main chamber.

3. Results and discussion

The top image in Fig. 2 shows an STM constant current topograph (CCT) image of 2.0 ML Ag deposited on TiO$_2$(110) in UHV conditions at ambient temperature. Three-dimensional (3D) hemispherical Ag clusters with relatively homogeneous sizes were observed, both on flat terraces and step edges. The Ag clusters have an average size of $\approx$4.8 nm $\times$ 2.6 nm (diameter $\times$ height), corresponding to $\approx$1900 atoms per cluster. In addition to the 3D Ag clusters, bare patches of substrate were also visible, indicating an island growth mode (Volmer–Weber growth mode) for Ag on TiO$_2$(110), consistent with our previous reports for other transition metals on TiO$_2$(110). XPS results (not shown) indicated a Ag binding energy of 368.1 eV, consistent with metallic silver.

After deposition of 2.0 ML Ag on the TiO$_2$(110) substrate and subsequent investigation by STM, the sample was transferred to the elevated-pressure reactor and exposed to 10.00 Torr O$_2$ at ambient temperature for 2 h. The sample was then transferred back to the UHV chamber and examined by XPS and STM. XPS results (not shown) indicated no Ag 3d$_{5/2}$ $E_b$ shift after O$_2$ exposure, consistent with other XPS studies of spent Ag catalysts. The bottom image in Fig. 2 presents an STM topograph of O$_2$-exposed Ag/TiO$_2$(110) and clearly reveals that the exposure dramatically affected the cluster sizes. A bimodal size distribution of cluster sizes is apparent, with some clusters increasing in size while others decrease. Furthermore, a small increase (5–15%) in cluster density was observed, indicating that redispersion is occurring as well.

Fig. 3 shows the size distributions calculated from the STM images of Ag clusters before and after high-pressure O$_2$ exposure. Initially, Ag clusters exhibited a unimodal size distribution from 2.0 to 6.5 nm with a maximum diameter $\approx$5.0 nm. However, after O$_2$ exposure, a bimodal size distribution was observed, with one size domain from 1.0 to 5.0 nm and another from 5.0 to 11 nm. The smaller clusters in the range 1.0–5.0 nm have a higher density and a narrower size distribution, with an average Ag cluster size of $\approx$3.0 nm $\times$ $\approx$ 1.1 nm ($\approx$260 atoms). The larger clusters, however, have a lower cluster density and a broader size distribution, with an average size of $\approx$6.7 nm $\times$ $\approx$ 3.1 nm ($\approx$4200 Ag atoms per cluster). It is noteworthy that the total cluster volume before and after O$_2$ exposure calculated from the STM images agrees to within 10% error. Since Ag oxidation catalysts are typically used in elevated O$_2$ pressure conditions, an analysis of these induced morphological changes is of general interest to the catalysis community.
Fig. 2 STM images of Ag clusters on TiO$_2$(110) — (1 x 1) (2.0 V, 1.0 nA). The dosing flux is 0.125 ML min$^{-1}$ and the Ag coverage is 2.0 ML. Top: Fresh Ag/TiO$_2$(110) prepared at room temperature. Homogeneous Ag clusters are observed with a uniform size distribution. Bottom: 2.0 ML Ag/TiO$_2$(110) exposed to 10.00 Torr O$_2$ for 2 h at 300 K. The O$_2$ exposure results in a bimodal size distribution: certain clusters increase in size at the expense of other clusters.

In general, cluster growth of supported metal catalysts can proceed by two processes. First, clusters can migrate along the surface until they collide with other clusters, resulting in coalescence. Second, cluster growth can occur by intercluster transport, or Ostwald ripening, which is capillarity driven. In this case, the reduction of the total surface free energy by intercluster transport occurs such that certain clusters grow larger at the expense of other clusters.

Thus, in light of the bimodal size distribution observed following O$_2$ exposure, Ostwald ripening is likely the cause of the Ag cluster growth. Regardless of the cause, cluster growth results in catalysts with decreased active surface areas, leading to a decline in catalytic activity.

Intercluster transport of atomic (or molecular) species can occur by either surface diffusion along the substrate or vapor phase transport. Under vacuum or reducing conditions, the transport between Ag clusters can only occur in the form of free metallic Ag atoms, and the driving force should be related to the Ag vapor pressure. However, the Ag vapor pressure depends exponentially on the energy required to break Ag–Ag metal bonds and transfer a Ag atom to the vapor phase. 

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Fig. 3 The size distributions of 2.0 ML Ag/TiO$_2$(110) before and after 10.00 Torr O$_2$ exposure. Top: Fresh Ag clusters with a maximum volume $\approx$ 5.0 nm cluster diameter. Bottom: Ag clusters after O$_2$ exposure exhibiting a bimodal distribution with average cluster diameters of $\approx$ 3.0–3.5 nm and 6.5–7.0 nm, respectively.

phase, i.e., the sublimation energy, $\Delta_{\text{subb}}H(\text{Ag})$, which is $\approx$ 285 kJ mol$^{-1}$. Obviously, such a high energy barrier suggests that intercluster transport by free Ag atoms will be very slow at room temperature. This result is in accordance with our STM observations that Ag clusters are generally stable in UHV conditions.

In an oxidizing environment, the situation is quite different. For example, Wynblatt$^{16}$ showed that growth of Pt particles in O$_2$ environments occurred through the formation of volatile PtO$_2$. Platinum oxide has a lower sublimation energy than platinum metal and therefore serves as the mechanism by which intercluster transport occurs. Unfortunately, to the best of our knowledge, no vapor pressure or sublimation energy data is available for silver oxide, rendering it difficult to directly compare such values with Ag metal. However, it will be shown that the formation of Ag$_2$O from Ag particles in 10.00 Torr O$_2$ is at least expected thermodynamically and thus may account for the intercluster transport discussed above.

Thermodynamically, Ag can form silver oxide (Ag$_2$O) by reaction with oxygen at room temperature. This can be illustrated by considering the following simple reaction

$$2\text{Ag}(s) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{Ag}_2\text{O}(s)$$

which has a negative standard free energy of formation of Ag$_2$O ($\Delta G_{298} = -11.2$ kJ mol$^{-1}$) at room temperature. The equilibrium constant $K_p$ for the above reaction can be expressed as

$$K_p = a_p a_{\text{Ag}}^{-2} (p_0)^{-1/2}$$

where $a_p$ and $a_{\text{Ag}}$ are the activities of Ag$_2$O and Ag, respectively (both values are unity), and $p_0$ is the equilibrium partial pressure of oxygen. Substitution of $K_p$ into the standard $\Delta G$ equation yields

$$\Delta G_T = \frac{1}{2}RT \ln p_{\text{O}_2}$$

where $T$ is the absolute temperature and $R$ is the universal gas constant. Ag oxidation can only occur under the present conditions if the partial pressure of O$_2$ in the cluster environment is higher than the $p_{\text{O}_2}$ value in eqn. (4) for $T = 298$ K. By substituting $\Delta G_{298} = -11.2$ kJ mol$^{-1}$ into eqn. (4), the equilibrium oxygen partial pressure $p_{\text{O}_2}$ was calculated to be $1.23 \times 10^{-4}$ atm (0.094 Torr). Since the partial pressure in the cluster environment (10.00 Torr) is higher than the equilibrium oxygen partial pressure at 300 K, then the oxidation of bulk Ag is thermodynamically allowed.

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An additional effect that must be considered is the influence of the Ag cluster curvature on the free energy. The decrement $\Delta g$ in free energy due to cluster curvature is given by

$$\Delta g = 2\sigma M/(\rho r)$$

(4)

where $\sigma$ is the surface energy, $M$ is the atomic weight, $\rho$ is the density and $r$ is the cluster curvature radius.\(^1\) At room temperature, taking $\sigma = 1400$ erg cm\(^{-2}\), \(^1\) and $\rho = 10.5$ g cm\(^{-3}\), $\Delta G_{298}(r)$, the standard free energy of formation of Ag$_2$O for Ag clusters with curvature radius $r$ (in nm), is given by

$$\Delta G_{298}(r) = \Delta G_{298} - \Delta g = -11.2 - 28.8/r(\text{kJ mol}^{-1})$$

(5)

For an average cluster diameter of 5.0 nm ($r = 2.5$ nm), the value of $\Delta G_{298}(r)$ is doubled ($\Delta G_{298}(r) = -22.7$ kJ mol\(^{-1}\)). As the cluster size decreases further to 3.0 nm ($r = 1.5$ nm), the absolute $|\Delta G_{298}(r)|$ value increases by a factor of 1.7. Therefore, the driving force for oxidation of Ag nanoclusters is increased significantly at room temperature when accounting for cluster curvature effects. While this analysis shows that Ag$_2$O formation from Ag and O$_2$ is possible at room temperature, information about the rate of Ag$_2$O formation is not available.

4. Conclusions

In summary, Ag nanoclusters on TiO$_2$(110) are likely to form Ag$_2$O when exposed to 10.00 Torr O$_2$ at room temperature. Ag atoms in the form of volatile oxide molecules can thus be transported between clusters at higher rates than metallic Ag atoms under vacuum or reducing conditions. In principle, this somewhat volatile oxide may diffuse more easily along the surface of the support, or through the vapor phase, from higher-energy sites to lower-energy sites. Consequently, Ostwald ripening is observed when the Ag nanoclusters are exposed to oxygen. Evidence for redispersion through the vapor phase, from higher-energy sites to lower-energy sites. Consequently, Ostwald

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