Scanning tunneling microscopy of gold clusters on TiO$_2$(110): CO oxidation at elevated pressures

A. Kolmakov, D.W. Goodman *

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

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Abstract

The in situ imaging of individual supported nanoparticles with scanning tunneling microscopy at elevated temperatures while changing the ambient pressure of the reactants over ≈10 orders of magnitude is demonstrated. Specifically, the morphological changes of the gold–titania interface have been studied under CO oxidation reaction conditions. The changes in metal cluster size and titania surface re-growth have been observed during pressure excursions of the CO and O$_2$ reactants from 1 × 10$^{-8}$–665 Pa. © 2001 Elsevier Science B.V. All rights reserved.

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There are many fundamental and applied reasons for studying the stability of deposited nanoparticles during their exposure to elevated temperatures and realistic reactant pressures. In microelectronics such studies are relevant to the reliability and durability of state-of-the-art nano-sized junctions and active elements. In catalysis, deactivation of the active metal component is directly related to the morphological and compositional changes of the dispersed nanoparticles under typical operating conditions. For more than two decades surface analytical studies of supported metal nanoparticles in ultrahigh vacuum (UHV) have investigated processes such as particle sintering known to occur in the more complex catalytic systems. However the limitations of UHV studies have become apparent in that the interaction of the reactants with the catalyst surface, the activity of the catalyst, as well as the structure and morphology of the surfaces are often dramatically altered at elevated pressures [1–3]. The importance of elevated pressures has been documented recently in ex situ scanning tunneling microscopy (STM) studies of noble and transition metal clusters supported on oxides exposed to even 100 Pa of a reactive atmosphere [4,5]. Since such environmental effects cannot be addressed with traditional surface science techniques operating at UHV conditions, the term “pressure gap” has been used to refer to the inaccessibility of certain phenomena outside specific pressure conditions. The applicability of STM in UHV and elevated pressures provides a means of bridging the “pressure gap” between UHV studies and the environments typically used with technical catalysts.

*Corresponding author. Tel.: +1-979-845-0214/409-845-0214; fax: +1-979-845-6822/409-845-6822.
E-mail address: goodman@mail.chem.tamu (D.W. Goodman).

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There have been recent attempts to explore the influence of pressure with in situ STM using metal single crystal surfaces specifically to gain insight into surface reconstruction induced by elevated pressures [1,2]. However, analogous studies of more realistic systems such as oxide-supported metal nanoparticles have not been reported, although the underlying difficulties of performing such experiments have been described recently [6].

In this letter, the first successful results to target a selected area of interest on an oxide-supported metal catalyst with STM while modifying the reactive gas pressure over 10 orders of magnitude are described. These experiments demonstrate the feasibility of imaging individual supported nanoclusters at realistic reaction temperatures and pressures.

Gold clusters dispersed on a titania surface were chosen for this study. The interest in nanosized clusters of Au has grown in recent years due to the unique catalytic activity exhibited by gold nanoparticles [7,8]. In situ STM imaging of these clusters over a wide pressure range should provide valuable insights into the deactivation and regeneration of analogous industrial catalysts.

The experimental setup consists of a UHV analysis/preparation chamber attached to a second chamber housing a commercial (RHK VT-UHV-300) variable temperature STM. Both chambers have base pressures of $2 \times 10^{-8}$ Pa; the STM chamber can be pressurized with reactive gas to 133 kPa. The variable temperature STM utilizes a “walker” scan head mounted over a sample holder, an arrangement that minimizes temperature- and pressure-induced drifts. High-resolution scans were carried out using a central piezo tube with an attached tip. While imaging, the UHV-STM chamber can be pressurized and the sample heated to 600 K radiatively using a 30 W halogen lamp. The STM chamber can be evacuated using sorption pumps while maintaining high vacuum conditions.

The TiO$_2$(110) crystals (Commercial Crystal Laboratories) were reduced using multiple sputtering-annealing cycles; after these cycles, the imaged surface was light blue, exhibited a $1 \times 1$ structure, and showed no measurable impurities via AES. Au clusters were grown by vapor deposition from a calibrated metal doser with a deposition rate of $\approx 0.01$ monolayer equivalents (MLE) per second. The gas mixture of CO:O$_2$ (Matheson and Messer, respectively, both research grade) was further cleaned (particularly from water) prior to exposure via maintaining the gas reservoir at $\approx 200$ K. The reactant mixture was slowly leaked into the STM chamber to assure homogeneous heat exchange within the microscope while maintaining the sample at 450 K [7,8]. The thermal drift was sufficiently small to allow the selected areas to be imaged over the entire pressure range. The STM images were acquired at the indicated conditions of pressure and temperature by holding the tunneling parameters constant for each pressure excursion.

Small noble metal clusters are known to be weakly bound to the TiO$_2$ surface and are therefore easily disturbed by the STM, an affect enhanced while imaging in ambient gas [6]. Therefore, at the expense of resolution, the images for this study were typically acquired at an elevated impedance of $\approx 10$–50 GΩ to insure large tip-surface separation. However, even with these precautions, adhesion of individual clusters to the tip occurs. Therefore, the apex of the tungsten tip is assumed to be coated with Au, enhancing its chemical inertness.

In Fig. 1, the evolution of a 0.2 MLE Au deposit on titania is shown as a function of CO:O$_2$ pressure/exposure at 450 K. Under UHV conditions (Fig. 1(A)) uniform gold clusters with apparent cluster sizes ranging from 1–5 nm in diameter and 0.2–0.8 nm in height are visible on the TiO$_2$(1 × 1) surface. This surface morphology is stable for hours of scanning at 450 K. The CO:O$_2$ mixture causes several noteworthy changes at pressures above 1 Pa and exposures exceeding $10^5$ L (Fig. 1(C, D)). First, the Au clusters initially have a bimodal diameter peaking at $\approx 1$ and 4 nm, respectively (see Fig. 1(A)), each of which behave differently upon gas treatment. For the majority of the “large” Au clusters, the apparent size increases $\approx 25\%$ upon the treatment while the cluster density remains constant (compare Fig. 1(A) and (D)). A fraction of the “smaller” clusters decrease in size or vanish completely (note marked clusters at Fig. 1(C) with (D), (E)). The gas-induced disappear-
Fig. 1. 100 × 100 nm² CCI STM images of Au clusters supported on TiO₂(1 × 1) at 450 K. Clusters that are moved or disappear because of tip-cluster interactions are marked with squares; clusters that change in size with time are highlighted with circles. The conditions for each image are: (A) UHV; (B) P_{mixture} = 10⁻³ Pa; (C) P_{mixture} = 1 Pa; (D) P_{mixture} = 360 Pa, total exposure (TE) ~ 2 × 10⁷ L; (E) P_{mixture} = 720 Pa, TE ~ 3 × 10⁸ L; (F) P_{mixture} = 720 Pa, TE ~ 1.4 × 10⁹ L.

ance of the smallest clusters may be due to the increase in the rate of the lateral mass transport among the clusters, an effect reported in ex situ STM studies of similar systems exposed to elevated pressures of reactive gases [4,5,9]. Alternatively, the preferential adhesion of a fraction of the smallest clusters to the STM tip can take place. An apparent increase in the overall cluster size, on the other hand, may arise because of a decrease in the tunneling probability upon O₂ and/or CO adsorption on reduced titania. This latter effect can be seen by comparing the I(V) curves measured for cluster-free areas of the as-prepared TiO₂ surface and those measured for the same surface following prolonged gas treatment (Fig. 2(A)). The adsorbate, as an electron acceptor, may react with the surface Ti³⁺, eliminating tunneling from the Ti³⁺ induced gap states, and thus effectively widening the surface band gap. In the constant current imaging mode, a decrease in tunneling probability,
The apparent cluster size is also a consequence of the Schottky-like barrier that forms at the cluster–semiconductor interface [10]. This interaction leads to a change in the apparent cluster size with sample bias (see Fig. 2(B)). This effect is beyond the scope of this letter and is the subject of a forthcoming publication [11].

Fig. 2. (A) Scanning tunneling spectroscopy $I(V)$ over as-prepared titania (light curve) and after $\approx 10^{11}$ L CO:O$_2$ exposure at 450 K (bold curve) measured at 300 K. Each curve is an average of 150 separate measurements. (B) A line profile over an area of the sample exposed to 665 Pa of CO:O$_2$ mixture as a function of sample bias. The atomic step shows no bias dependence whereas the cluster dimensions exhibit marked bias dependence.

seen as a reduction in the tunneling current in the $I(V)$ curves of Fig. 2(A), leads to a closer approach of the tip to the surface and therefore alters the baseline for the apparent cluster size measurement. In addition, this closer approach of the tip caused by the adsorbate-induced reduction of the tunneling probability also facilitates adhesion of the smallest noble metal clusters to the tip. This latter effect was noted in our previous work [6] and was assumed to arise from attractive forces between the tip and the clusters and to a weakening of the cluster–oxide interaction upon surface oxidization.

Fig. 3. A $50 \times 50$ nm$^2$ image of the same area taken at 450 K: (A) under UHV conditions; (B) during 665 Pa CO:O$_2$ mixture exposure. The clusters removed due to tip effects are marked by squares. The circles indicate those clusters exhibiting gradual reduction in size.
The reduction in cluster size is apparent in the evolution of specific clusters from UHV to elevated pressures. In Fig. 3 a selected area is shown in (A) for UHV conditions and in (B) for 665 Pa of the reaction mixture. The clusters marked with circles exhibit a gradual decrease in size with respect to their neighbors; those clusters that disappear due to tip–cluster interaction are marked with squares. There are noteworthy parallels between the instability of the small Au clusters, their catalytic activity, and the change in their catalytic activity with time. Previous studies [8] have shown that Au clusters of \( \approx 3 \) nm are optimum as CO oxidation catalysts, and that reaction-induced sintering of these small clusters is a mechanism for the loss of activity with time. Although questions remain regarding the precise details of the growth in cluster size with exposure to reactants, these data do not support a deactivation mechanism in which the Au clusters are covered by titania overgrowth as previously seen for Pd clusters [12].

In summary, the successful in situ imaging of titania supported gold clusters at elevated pressures and temperatures demonstrates the feasibility of using STM for studying model catalysts under realistic reaction conditions. Pressure-induced morphological changes were observed for the individual gold nanoclusters and selected titania-support areas while changing the gas pressure over 10 orders of magnitude. The importance of decoupling pressure-induced artifacts from real effects is highlighted. Small gold clusters and the reduced support appear to be unstable under reaction conditions. Both phenomena are presumably responsible for reducing the number of active sites and thus for the previously reported loss of catalytic activity.

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References