Direct Visualization of Au Atoms Bound to TiO$_2$(110) O-Vacancies

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ABSTRACT: Au nanoparticles supported on reducible metal oxide surfaces are known to be active catalysts for a number of reactions including CO oxidation and hydrogen production. The exact choice of a metal oxide support has been shown to have a marked impact on activity, suggesting that interactions between Au and the support play a key role in catalysis. For TiO$_2$, a model substrate for Au catalysis, it had been thought that bridging oxygen vacancies are involved in binding Au atoms to the (110) surface based on indirect evidence. However, a recent scanning transmission electron microscopy study of single Pt atoms on TiO$_2$(110) suggests that subsurface vacancies are more important. To clarify the role of bridging or subsurface vacancies we employ scanning tunneling microscopy to determine the bonding site of single Au atoms on TiO$_2$(110). Using in situ deposition as well as a manipulation method, we provide definitive evidence that the bonding site is atop surface oxygen vacancies.

INTRODUCTION

The nature of the interaction of metal nanoparticles and their metal oxide supports remains a key area of research in catalysis. In particular, gold nanoparticles supported on TiO$_2$ have received considerable attention following the discovery that they are an effective low-temperature oxidation catalyst. As a model catalyst, Au adsorption on rutile TiO$_2$(110) has been extensively studied because this substrate is the most well-characterized metal oxide substrate. When reduced, TiO$_2$ (110) contains point defects in the form of oxygen vacancies (O$_{\text{b-vac}}$) as well as Ti interstitial atoms in the bulk. O$_{\text{b-vac}}$, in particular, are a widely studied aspect of TiO$_2$ fundamental catalysis because they are reactive sites on the surface and in many cases they act as bonding sites for surface adsorbates.

A key feature of the Au/TiO$_2$ system that remains controversial is the bonding site of individual Au atoms on the surface (Au$_1$). This is potentially important in connection to single atom catalysis, which has been demonstrated for a number of systems, most recently for Au atoms on carbon. On TiO$_2$(110), Au$_1$ has been shown to be stable up to at least 600 K. After soft landing Au$_1$, Tong et al. observed bonding of Au atoms to the bridging oxygen row using scanning tunneling microscopy (STM) and assigned the adsorption site to a bridging O$_{\text{b-vac}}$. On cooling to 300 K they observed a reversible shift of adsorption site to the Ti row, assigning the adsorption site as atop a five-fold coordinated Ti site ($\text{Ti}_5\text{c}$). This was interpreted as a displacement of Au$_1$ by interaction with adventitiously coadsorbed water at the lower temperature. This is in line with previous spectroscopic work and STM measurements.

Although the STM results referenced above clearly observe Au$_1$ associated with the bridging O row, there is no direct evidence of bonding to O$_{\text{b-vac}}$. On the contrary, several density functional theory (DFT) calculations suggest that O$_{\text{b-vac}}$ is the preferred site. More recent results have challenged the assignment of O$_{\text{b-vac}}$ to the binding site of noble metals. In particular, aberration-corrected scanning transmission electron microscopy (STEM) has been used to image Pt$_1$ on TiO$_2$(110). In their paper, the authors conclude that Pt$_1$ occupies in-plane O vacancies. Theory predicts that the lowest energy site of Pt$_1$ atoms on reduced TiO$_2$(110) is the same as for Au$_1$, that is O$_{\text{b-vac}}$. Hence the implication of the STEM work is that Au$_1$ will also occupy in-plane O vacancies. If this was correct, then the discrepancy between DFT and experiment could arise from a dominance of kinetic effects. This has recently been demonstrated for a related system, Au-CeO$_2$(111), where kinetic effects prevent the occupation of oxygen vacancies by Au$_1$. Here we demonstrate that this is not the case for Au$_1$ on a reduced rutile TiO$_2$(110) surface ($\text{r-TiO}_2$). We present direct evidence that single Au atoms bind at O$_{\text{b-vac}}$ through a comparison of STM images of the same area on the surface before and after dosing Au$_1$. We have also employed a method to selectively displace Au atoms using voltage pulses from an STM tip, thereby exposing the underlying O$_{\text{b-vac}}$.

EXPERIMENTAL METHODS

STM measurements employed two UHV Omicron instruments. One is a low-temperature bath cryostat machine (LT-
STM) operated at 78 K with a base pressure of $3 \times 10^{-11}$ mbar. The second is a variable temperature microscope (VT-STM) operated at 300 K with a base pressure $5 \times 10^{-11}$ mbar. A rutile TiO$_2$ (110) (1 x 1) single-crystal (MaTeck) sample was prepared by successive cycles of argon ion sputtering and annealing to 1000 K. The sample cleanliness and long-range order were confirmed using X-ray photoelectron spectroscopy (XPS) or Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED), respectively. Surfaces prepared in this manner typically have a coverage of ~5% ML of O$_{\text{v}}$vacs (where 1 monolayer is the number of surface unit cells).

Au was deposited in situ onto an as-prepared TiO$_2$(110) surface present in the sample stage of the VT-STM at room temperature. Deposition was performed using a line-of-sight electron beam evaporator (Omicron EFM). The STM tip was retracted prior to deposition. In the LT-STM, Au was deposited onto as-prepared TiO$_2$ (110) at room temperature using a Au rod wrapped around a tungsten filament, which was resistively heated to induce Au sublimation. The presence of Au on the TiO$_2$ substrate was confirmed using XPS. In both systems, STM measurements were carried out in constant current mode using an electrochemically etched W tip conditioned by degassing at 500 K and voltage pulses in STM. There were no significant differences in Au coverage or dispersion seen in STM images recorded at 78 and 300 K.

**RESULTS AND DISCUSSION**

Figure 1a shows an STM image of the as-prepared TiO$_2$ (110) surface recorded after deposition of 0.08 monolayer (ML) of Au. Au coverage was determined by measuring the average density of Au atoms on the surface via STM and dividing by the density of a single (111) layer of bulk gold, that is, 1 ML = 1.387 x $10^{15}$ Au atoms cm$^{-2}$.

In STM, the TiO$_2$ (110) surface is characterized by bright rows of five-fold coordinated Ti$^{4+}$ (Ti$_{5c}$) and dark rows of two-fold bridging O$_2^{2-}$ (O$_b$) running along the [001] direction. Five distinct types of features appear evenly distributed over the surface. The three smallest features are all centered over the O$_b$ rows. The first appears as a small horizontal line (yellow circle), whereas the two larger features are more circular (blue circle and green ellipse). Such features are well described in the literature and are attributed to O$_{\text{v}}$vacs and OH$_b$, respectively. A model showing these features is shown in Figure 1b. The two remaining unidentified features in Figure 1a are not typical of STM images from r-TiO$_2$ (110) and can be attributed to deposited Au species. The first (highlighted as white solid circles in Figure 1a) appears centered over the O$_b$ rows on the surface with an average height of 193 ± 60 pm. The second (highlighted as white dashed circles in Figure 1a) is larger, spanning multiple O$_b$ rows in the [110] direction with an average height of 233 ± 10 pm. The larger Au species are found centered over either O$_b$ or Ti$_{5c}$ rows. Using STM in conjunction with DFT calculations, Matthey et al. identified the smallest Au species present on an Au-deposited r-TiO$_2$ (110) to be Au$_{1.8}$. The second smallest species they assign as Au$_3$. A model showing these features is shown in Figure 1b. The two remaining unidentified features in Figure 1a are not typical of STM images from r-TiO$_2$ (110) and can be attributed to deposited Au species. The first (highlighted as white solid circles in Figure 1a) appears centered over the O$_b$ rows on the surface with an average height of 193 ± 60 pm. The second (highlighted as white dashed circles in Figure 1a) is larger, spanning multiple O$_b$ rows in the [110] direction with an average height of 233 ± 10 pm. The larger Au species are found centered over either O$_b$ or Ti$_{5c}$ rows. By direct comparison of our data with the previous work, the smallest Au species observed in Figure 1a are assigned as Au$_1$ and the larger ones to Au$_3$.

To unambiguously identify the binding site of Au$_1$, we performed in situ deposition of Au and imaged the same region of the r-TiO$_2$ surface before and after deposition. This was achieved by collecting an STM image of r-TiO$_2$ in an Omicron VT-STM instrument. The STM tip was then retracted and Au was deposited onto the imaged region using an in situ electron-beam evaporator that points to the STM stage. After deposition, the STM tip was reapproached to exactly the same position. Both the Au deposition and STM measurements were carried out at 300 K. As shown in Figure 2, after
deposition some O_b-vacs that were on the r-TiO_2 are now filled by individual Au atoms (marked by circles in Figure 2a,b). Similar entities appear centered over Ti_5c rows but are much less frequent (<10%).

In addition, low-temperature measurements were also performed using an Omicron LT-STM system. At 78 K no Ti_5c-centered Au species were observed at all. On this basis, we conclude that O_b-vacs are the most stable binding sites for Au_1 on the r-TiO_2 surface.

To provide further evidence that Au_1 binds to O_b-vacs, STM tip pulsing was used to laterally manipulate Au_1 on r-TiO_2. STM tip-induced manipulation has been widely employed to form nanostructures on planar surfaces, and this field is reviewed in ref 15. To ensure stability and reproducibility, pulsing was performed at 78 K. Figure 3 shows atomically resolved STM images of Au_1 on r-TiO_2 (110) taken before (Figure 3a) and after (Figure 3b) application of a 100 ms tip pulse over the Au_1 species at a sample bias of −2 V. Arrows indicate the directions of Au_1 displacement. Three spectator adsorbates are present in the images, namely, a single and two double OH groups. The bright (Ti) rows run in the [001] direction.

![Image](image_url)

Figure 3. STM images (V = +1.2 V, I = 10 pA) of Au_1 on r-TiO_2(110) at 78 K showing its displacement from (a) one O_b-vac to (b) another O_b-vac site, induced by a 100 ms tip pulse over the Au_1 species at a sample bias of −2 V. Arrows indicate the directions of Au_1 displacement. Three spectator adsorbates are present in the images, namely, a single and two double OH groups. The bright (Ti) rows run in the [001] direction.

complex is likely to have been stabilized by the cryogenic conditions used (78 K).

To determine the underlying mechanism of Au_1 displacement, a detailed statistical analysis of pulsing events was performed. This follows a methodology used previously to investigate tip-induced H desorption from Si(100)-2×1:H17 and TiO_2(110)−OH.18 During a tip pulsing experiment the STM tip is first centered over an Au_1 species. By monitoring the tunneling current (I_T) for the duration of each pulse, a plot of I_T(t) is created (Figure 5 inset). For each pulse an I_T set point is reached and held constant by the feedback loop of the STM. During manipulation, a peak in the I_T(t) plot can be seen. This peak corresponds to the sudden displacement of the Au_1 species. To eliminate the possibility that this O_b-vac was generated as a consequence of tip pulsing, the bare O_b rows using −2 V tip pulses; however, in their work they use a pulse duration of 1 s compared with the 100 ms pulses applied here.16 Hence the Au_1 manipulation experiment also points to bonding with O_b-vac.

In addition to movement from one O_b-vac to another, Au_1 could be manipulated from an O_b-vac onto a Ti_5c site (Au_1-Ti) following application of a tip pulse (see Figure 4). The formation of these Au_1-Ti species was observed in a minority of events. After several STM scans (~20 min) the Au_1-Ti were seen to spontaneously move onto nearby O_b-vacs sites becoming Au_1-O_b-vac. After moving from Au_1-Ti to Au_1-O_b-vac no subsequent changes were observed.

This supports the view that Au_1 binds more strongly to O_b-vac than to Ti_5c sites.8,9 In this case, the observed Au_1-Ti peak is reached and held constant by the feedback loop of the STM. During manipulation, a peak in the I_T(t) plot can be seen. This peak corresponds to the sudden displacement of the Au_1 beneath the tip. The increase in tip−sample distance caused by the now absent Au_1 decreases I_T sharply before the feedback loop corrects for the change by bringing I_T back to the initial set point. The pulse duration required to induce movement can be determined from the position of the excursion in I_T. This process was repeated multiple times (~60) for each set of pulsing parameters used in this work. After plotting the resulting data in histogram form, an exponential decay was fit to

![Image](image_url)

Figure 4. (a) STM images (V = +1.2 V, I = 10 pA) of Au_1 on r-TiO_2(110) at 78 K before (a) and after (b) STM tip-induced displacement of Au_1 to a Ti_5c row induced by a −2 V, 100 ms tip pulse centered above Au_1. The TiO_2(110) surface lattice has been overlaid on the image, where intersections in the grid indicate Ti_5c positions. Arrows indicate the movement of Au_1 from an O_b-vac to a Ti_5c site. The bright (Ti) rows run in the [001] direction.

![Image](image_url)

Figure 5. Histogram showing the distribution of Au_1 displacement times for tip pulses of V = −1.8 V and I = 10 pA. The red line represents an exponential fit to the distribution of statistically independent events. The inset is an example of an individual I_T trace used to compile the histogram where I_T is the set point of the pulse (10 pA) and t is the pulse duration prior to Au_1 displacement.
the data to yield the average value of \( \tau \) for each pulsing parameter, an example being shown in Figure 5. For each plotted histogram, bin widths were varied, within a reasonable range, such that the resulting change in \( \tau \) could be factored into the error of each average value determined.

To confirm that the measured distribution of Au\(_1\) displacement times does indeed follow an exponential decay, a semilog plot of \( \ln N(t) \) was created for each data set (Figure 6).

![Figure 6](image)

**Figure 6.** Plot of \( \ln N(t) \) versus time for the data shown in Figure 5. The red line shows a linear fit to the data. The last eight points of the plot have been attributed to random noise and are omitted from the fitting. From the slope of the linear fit, \( \tau \) was determined to be 17.4 ms. The fitting from this plot was used to refine the exponential fitting to the histogram shown in Figure 5 and hence the value of \( \tau \).

The displacement yield (events per electron), \( Y \), was determined using the average value of \( \tau \) measured for each pulsing parameter. \( Y \) values were calculated for a range of pulsing currents and voltages and were plotted as a function of \( I_T \). The relationship between \( Y \) and \( I_T \) was then used to determine the displacement reaction order, that is, the number of principal electrons involved in the dissociation of a single Au\(_1\) from an O\(_{h}\) vac (Figure 7). Because for an n-electron process \( Y \propto I_T^{(n-1)} \), the gradients observed in Figure 7, which are approximately unity, indicate a two-electron vibrational ladder-climbing process. Such a mechanism is typical for adsorbates on semiconductors\(^{15}\) and has been proposed previously for STM tip-induced dissociation of H from TiO\(_2\)(110)–OH.\(^{18}\)

![Figure 7](image)

**Figure 7.** Double-logarithmic plot of displacement yield, \( Y \), as a function of tunneling current, \( I_T \). Solid circles, squares, triangles, and rhombi represent the measured yields of Au\(_1\) displacements at different pulse voltages (labeled). Lines show power-law fits to the experimental data, with exponents (\( \alpha \)) given for each pulse voltage.

### CONCLUSIONS

The direct evidence provided here for bonding of gold atoms to bridging oxygen vacancies on TiO\(_2\)(110) is clearly in accord with the predictions of DFT calculations.\(^{6,9}\) There is, however, a marked disagreement between this work and the conclusions of a scanning transmission electron microscopy study of platinum atoms on TiO\(_2\)(110).\(^{12}\) In this previous work, bond sites atop subsurface vacancies were proposed, with no observed bonding to bridging oxygen vacancies. A likely cause of this difference is that the surface in the previous work was hydroxylated, a state that is known to promote occupation of Ti\(_{oc}\) sites.\(^{5,8}\) Hence, our result removes an important discrepancy in the literature between theory and experiment and reinstates the importance of bridging oxygen vacancies in the catalytically related chemistry of TiO\(_2\).

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