Catalysis by Supported Gold Nanoclusters

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INTRODUCTION

The physical and chemical properties of supported Au clusters are markedly sensitive to cluster size and morphology. To investigate the origin of the unique properties of nanosized Au clusters, model catalysts consisting of Au clusters of varying sizes have been prepared on single crystal TiO$_2$(110) and ultrathin films of single crystalline TiO$_2$, SiO$_2$, and Al$_2$O$_3$. The morphology, electronic structure, and catalytic properties of these supported Au clusters have been investigated using an array of surface analytical techniques with particular emphasis to the unique properties of clusters <5.0 nm in size. These studies illustrate the novel and unique physical and chemical properties of nanosized supported metal clusters.

BACKGROUND

Unique electronic and chemical properties are known to develop in solids when the dimensions of the solid reach the nanoscale.[1–3] These changes, which include discrete electronic structures, modified physical structures, and altered chemical reactivities, manifest themselves as new physical and chemical properties not observed in the “bulk” form of the material. Developing an understanding and ability to control the key features of nanoscale catalysts are daunting scientific challenges, yet could lead to the long-sought goals of optimum catalytic activities combined with highly specific selectivities.

It is well established that ultrasmall metal clusters on supports have catalytic properties distinct from those properties of large bulk-like particles, as illustrated by the selective oxidation of propylene to propylene oxide by gold,[4] alkene and arene hydrogenation catalysts,[5] and CO oxidation.[6–8] In these examples, the catalytic properties improve as the clusters become smaller. On the other hand, a reduction in size of the metal cluster can lead to less desirable catalytic properties as seen for ammonia synthesis on iron.[9] Various explanations have been offered to account for the unique properties of nanoscaled metal catalysts,[6–8] however, much remains to be understood. Clearly, experimental and theoretical studies will be required to develop an in-depth understanding of the unique catalytic properties of limited dimensional solids.

The complexity of high surface area technical catalysts makes developing an atomic-level understanding an extremely challenging problem. Surface science studies offer atomic-level information regarding the details of catalytically relevant surfaces, but have traditionally focused on well-defined, single-crystal metal surfaces to address the relationship between reactivity and surface morphology. Single crystal studies, however, obviously do not address the size-dependent structural and electronic properties that are unique to metal nanoparticles. Toward the goal of understanding the properties of supported metal clusters, several groups have begun investigations of metal clusters supported on planar oxide surfaces.[10–14]

Our group, in particular, has focused extensively on the unique properties of supported gold clusters for selective oxidation reactions.[15]

Our approach to studying supported metal clusters has been to combine ultrahigh vacuum (UHV) surface analytical methods with an elevated pressure reactor system shown schematically in Fig. 1. The design has been described in detail.[14,16] This arrangement allows pressures to 1 bar in the high-pressure cell without significantly altering the vacuum integrity of the UHV chamber. This arrangement facilitates the acquisition of kinetic data at elevated pressures using a conventional gas chromatograph. Polarization modulation infrared reflection absorption spectroscopy (PM-IRAS) is available as a probe of surface species present under reaction conditions.[13]

The oxide surfaces used as supports in these studies were either a TiO$_2$(110) single crystal (Commercial Crystal Laboratories) or single crystalline TiO$_2$, Al$_2$O$_3$, or SiO$_2$ thin films synthesized on a refractory metal substrate. Thin film TiO$_2$ was deposited onto a Mo(110) single crystal.[17] Similarly, the SiO$_2$ and Al$_2$O$_3$ supports were epitaxially grown as thin films deposited onto Mo(110)[18–20] and Re(0001)[21–23] substrates, respectively. Details of the sample mounting, cleaning, etc. can be found elsewhere.[14]

The Au doser was constructed by wrapping high-purity Au wire (99.99%) around 0.010-diameter tungsten filaments (H&R Cross), which were then resistively heated in vacuum by passing current through the filament wires. The Au wire wrapping was melted and thoroughly outgassed to
remove impurities prior to use. The Au flux was calibrated via integrating the Au temperature-programmed desorption peak area from a Re(0001) substrate\textsuperscript{[15]} and also using the metal-to-substrate Auger intensity “break” to denote the first monolayer equivalent (ML).\textsuperscript{[24]} This article focuses on our recent studies on these model catalysts to understand the special properties that nanosized clusters exhibit with respect to a variety of catalytic reactions.

MODEL CATALYSTS:
RESULTS AND DISCUSSION

Synthesis

The synthesis of a typical model catalyst used in these studies is shown schematically in Fig. 2. The procedure begins with a refractory metal substrate, such as Mo, Ta, or Re, that has been cleaned by standard procedures and verified clean with surface analytical techniques. The structure of the substrate is chosen specifically to match the particular oxide film to be grown since crystal orientation and the nature of the interface or critical parameters in obtaining a high-quality film. A thin metal oxide film, typically 1–10 nm thick, is then deposited onto the metal substrate by vapor deposition of the parent metal in an O\textsubscript{2} environment. Thin films of SiO\textsubscript{2},\textsuperscript{[18–20]} Al\textsubscript{2}O\textsubscript{3},\textsuperscript{[21–23]} TiO\textsubscript{2},\textsuperscript{[17,25]} MgO,\textsuperscript{[26–29]} NiO,\textsuperscript{[30–33]} and Fe\textsubscript{3}O\textsubscript{4}\textsuperscript{[34]} have been prepared using this methodology. Finally, metal clusters are formed on the oxide thin film by vapor depositing the metal of choice. By the judicious control of the metal deposition parameters, metal clusters of varying size can be routinely achieved.\textsuperscript{[14]} A variety of oxide/metal systems have been synthesized in our laboratories including Cu/SiO\textsubscript{2},\textsuperscript{[35,36]} Pd/SiO\textsubscript{2},\textsuperscript{[37]} Ni/SiO\textsubscript{2},\textsuperscript{[38]} Pd/Al\textsubscript{2}O\textsubscript{3},\textsuperscript{[39–41]} Cu/Al\textsubscript{2}O\textsubscript{3},\textsuperscript{[23,39]} Au/Al\textsubscript{2}O\textsubscript{3},\textsuperscript{[39]} Ni/Al\textsubscript{2}O\textsubscript{3},\textsuperscript{[42]} Au/TiO\textsubscript{2},\textsuperscript{[43]} and Pd/MgO.\textsuperscript{[43]}

Characterization

Scanning tunneling microscopy (STM) is an indispensable technique for characterizing planar surfaces with sufficient conductivity. Fig. 3a shows a CCT-STM micrograph of 0.25 ML Au deposited onto a single crystal TiO\textsubscript{2}(110).\textsuperscript{[8,15]} The deposition was performed at 300 K followed by an anneal of the TiO\textsubscript{2} surface to 850 K. Three-dimensional (3-D) Au clusters have average diameters of ~2.6 and ~0.7 nm height (corresponding to 2–3 atoms thick) and preferentially nucleate on step edges. Quasi-two-dimensional (2-D) clusters are characterized by heights of 1–2 atomic layers.\textsuperscript{[44]} An enlarged STM micrograph (150 x 150 nm\textsuperscript{2}) of a Au-covered (1.0 ML) TiO\textsubscript{2}(110) surface is shown in Fig. 3b. Hemispherical clusters with a narrow size distribution grow preferentially along the step edges with clusters on the flat terraces evident as well. At a Au coverage of 1.0 ML, more than 60% of the substrate is still metal-free and separated by mono-atomic steps, consistent with 3-D clustering or a Volmer–Weber (VW) growth mode.

Cluster size and density were studied as a function of metal coverage. With increasing Au coverage, the average cluster size (diameter) increases from 2.0 nm for 0.10 ML Au to 5.4 nm for 4.0 ML Au. However, the cluster density remains essentially constant at higher Au coverages (>1.0 ML). With an increase in the Au coverage from 0.10 to 0.25 ML, the cluster density...
increases by ~30%, with a further increase of ~50% from 0.25 to 1.0 ML Au. The cluster density reaches a maximum at ~2.0 ML where ~70% of the substrate surface is covered by Au clusters. At higher Au coverages, the cluster density declines because of cluster coalescence and agglomeration. Approximately 60% of the nucleating sites are populated at a coverage of 0.25 ML.[45]

The cluster size, in contrast to cluster density, increases continuously with Au coverage. Increasing the Au deposition from 0.10 to 2.0 ML increases the cluster size from 2.0 to 4.5 nm. A rapid increase in Au cluster size occurs for very low Au coverages (below 0.10 ML). Higher Au coverages correlate with a limited cluster growth. It is noteworthy that the increase in cluster volume is not proportional to the increase in cluster size. For example, a 22% increase in the average cluster diameter, from 3.7 (1.0) to 4.5 nm (2.0 ML), corresponds to an 80% increase in the average cluster volume. This correlation between Au coverage and Au cluster diameter demonstrates that vacuum deposition can produce a specific size range and shape of Au clusters for model catalyst studies.[45]

**Catalytic Properties**

A correlation has been observed between the Au cluster size and the catalytic activity for the partial oxidation of CO on Au/TiO₂(110)-(1 × 1). Fig. 4a shows a plot of the
activity for CO oxidation [expressed as (product molecules) \( \times \) (total Au atoms on surface sites)]\(^{-1}\) sec\(^{-1}\) or turnover frequency (TOF) at 350 K as a function of the size of Au clusters supported on a TiO\(_2\)(110)-(1 \( \times \) 1) substrate.\(^{[8,46]}\) The CO and O\(_2\) (1:5 mixture of CO:O\(_2\)) reaction was carried out over Au/TiO\(_2\) catalysts at 40-Torr total pressure.\(^{[8,46,47]}\) A thin film of TiO\(_2\) epitaxially grown on a Mo(100) substrate\(^{[47]}\) onto which Au clusters were deposited was used for the reaction kinetics measurements carried out in the reactor portion of Fig. 1. Scanning tunneling microscopy measurements of Au deposited onto a TiO\(_2\)(110)-(1 \( \times \) 1) single crystal were carried out in parallel with the kinetic measurements. The product (CO\(_2\)) was extracted from the reactor with a vacuum syringe, compressed and analyzed with a GC. For each point in Fig. 4a, a particular Au cluster size was prepared then subjected to the CO\(_2\):O\(_2\) reaction. The cluster sizes of the Au particles and coverage of the surface sites obtained from parallel STM imaging experiments were used to calculate the TOF. The activity of the Au/TiO\(_2\) catalysts exhibits a maximum TOF at an average Au cluster diameter of \(~3.5\) nm and decreases with an increase in diameter.

Fig. 4(b) is a histogram that shows the distribution of Au clusters with sizes ranging from 2.0 to 4.0 nm that are specifically two atoms thick (with diameters between 2.5 and 3.0 nm). The close correspondence between the maximum in the histogram and the maximum in the reactivity data is strongly suggestive that 2-atom-thick Au structures are optimally active for CO oxidation.\(^{[8]}\)

Fig. 5 shows a plot of the scanning tunneling spectroscopy (STS) band gaps measured over the cluster size regime used for the CO:O\(_2\) reactions of Fig. 4a. There is a clear correlation between the onset of catalytic activity and the observed metal-to-nonmetal transition in the supported Au clusters. The average Au cluster size where nonmetallic properties become apparent is 3.5 nm in diameter and 1.0 nm in height, corresponding to approximately 300 atoms per cluster. The square data in Fig. 5 are for those clusters two layers thick ranging in size from 2.0 to 4.0 nm in diameter and are those clusters which exhibit optimum catalytic activity for the CO oxidation reaction. The STS-measured band gaps of this group of clusters range from 0.2 to 0.6 V. These results demonstrate that electronic properties as a function of cluster size play a crucial role in defining the catalytic reactivity of small clusters.\(^{[8,46]}\)

### Adsorbate Binding Energies

Thermodynamic data regarding the adsorption of CO on Au/TiO\(_2\) catalysts with varying Au cluster sizes have been acquired with TPD using the well-known Redhead method\(^{[48]}\) and with IRAS using the Clausius–Clapeyron relationship.\(^{[49,50]}\) Results for these measurements are displayed in Fig. 6. CO adsorption on Au clusters larger...
than $\sim 4.0$ nm behaves as bulk Au. However, as the clusters become smaller, the heat of CO adsorption increases from 12 kcal mol$^{-1}$ to a maximum of 19 kcal mol$^{-1}$ for clusters $\sim 3.0$ nm in diameter.$^{[51]}$ Both sets of data in Fig. 6 suggest a marked increase in the adsorption energy with a decrease in cluster size; however, the results derived using the Clausius–Clapeyron relationship show a maximum that correlates remarkably close to the maximum observed in the reactivity measurements of Fig. 4a. A similar increase in the binding energy of O$_2$ with a decrease in the Au cluster size on TiO$_2$ has been observed recently.$^{[52]}$ In any case, clearly, the effects of cluster size on the adsorption properties of Au clusters are significant and likely a key to the altered catalytic properties displayed by ultrasmall Au clusters.

**Electronic Properties**

Fig. 7a shows the core level binding energies (BE) for the Au 4f$_{7/2}$ core level as a function of Au cluster coverage on a TiO$_2$(110) surface.$^{[15]}$ A +0.8-eV BE shift is evident for small clusters (0.02 ML, $\sim 2$-nm diameter) with a gradual

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**Fig. 6** CO heats of adsorption as a function of Au cluster size on a TiO$_2$(110) support. (View this art in color at www.dekker.com.)

**Fig. 7** (a) XPS binding energies of the Au 4f$_{7/2}$ core level as a function of Au cluster coverage (ranging from 0.02 ML—bulk) on TiO$_2$(110). (b) XPS binding energies for Au clusters on TiO$_2$ compared with Au clusters on SiO$_2$. The histogram takes into account the initial and final contributions to the observed overall BE shifts for Au on the two supports. (View this art in color at www.dekker.com.)
shift to the bulk value of Au $4f_{7/2} = 84.0$ eV \cite{53} with increasing cluster size (6 ML Au coverage, ~5-nm diameter). This increase in the BE with a decrease in cluster size is consistent with an earlier XPS study by Mason\cite{54} where the relative BE shifts of Au clusters (of varying sizes) supported on SiO$_2$ and Al$_2$O$_3$ were shown to depend upon the relative abilities of the substrate to screen the outgoing photoelectrons (final state effects). However, a comparison of the relative core level BE shifts of the Au/TiO$_2$ with the Au/SiO$_2$ shows that the BE shift for Au/SiO$_2$ is significantly larger (+1.6 eV) than that for Au/TiO$_2$ (+0.8 eV) in the transition from large to small cluster sizes. Differences in the magnitudes of these Au cluster core level BE shifts are believed to result from the relative strengths of the interaction of Au with the two metal oxide supports. Recent theoretical calculations\cite{55} predict an initial state reduction in the BE of 1.1–1.5 eV for the $4f_{7/2}$ core levels of Au on TiO$_2$. As shown in Fig. 7b, this relatively large initial state contribution to the core level shift of Au/TiO$_2$ relative to Au/SiO$_2$ is sufficient to account for the 0.8-eV difference observed for the total BE shifts measured for these two oxide supports. Fig. 8 shows the total density of states (TDOS) calculated for bulk Au compared with Au adsorbed on TiO$_2$.\cite{55} For adsorbed Au, the Au $d$ bands are much closer to $E_f$ because of the charge polarization in the interfacial region and a subsequent increase of the potential in the adlayer. Such a large energy shift of the Au $5d$ band toward the $E_f$, as discussed by Hammer and Norskov,\cite{56} should strongly alter the surface chemical properties of Au/TiO$_2$ from those of a clean bulk Au surface.

### Cluster Sublimation Energies

Temperature-programmed desorption (TPD) is a useful tool for obtaining detailed information on adsorbate-surface bonding and on adsorbate–adsorbate interactions, desorption kinetics, and determining binding energies of metals adsorbed onto surfaces. Temperature-programmed desorption binding energy determinations also allow for

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**Fig. 8** The total density of states (TDOS) of Au/TiO$_2$(110) in the top panel and the local density of states for Au on TiO$_2$(110) compared with Au in bulk Au(001). (View this art in color at [www.dekker.com](http://www.dekker.com).)
comparative estimations of admetal cluster size on different oxide supports. In a series of TPD spectra acquired for Au on SiO$_2$, a marked decrease in the Au cluster binding energies, denoted by the peak temperature maximum ($T_m$) in the TPD of the clusters, is observed.$^{[15]}$

The leading edge of the TPD peak maxima shifts to higher temperatures as the Au coverage increases. The inset shows a plot of the sublimation energy ($E_{sub}$) as a function of Au coverage, determined using the leading edge analysis.$^{[57]}$ At 0.2 ML, the $E_{sub}$ at $\sim 50$ kcal mol$^{-1}$ increases rapidly (with increasing Au coverage) to the bulk value at $\sim 90$ kcal mol$^{-1}$ at 5.0 ML. The decrease in $E_{sub}$ can be explained by the fact that an atom at the edge of a small cluster has fewer nearest neighbors than larger ones and hence desorbs more easily because of decreased surface tension.

The interaction of Au with TiO$_2$(001) has also been determined using the same approach. The results are shown in Fig. 9b. In this case, however, only a single desorption feature is observed with a common leading edge for all Au coverages. Using the leading edge analysis, the Au binding energy on TiO$_2$(001) is found to be 50 kcal mol$^{-1}$, considerably smaller than the Au bulk sublimation energy of 90 kcal mol$^{-1}$. This dramatic decrease of the sublimation energies at all cluster sizes, from the smallest to the largest, is clearly related to the strong interaction between the Au clusters and the TiO$_2$ support. This strong interaction leads to a greater degree of wetting of the TiO$_2$ by Au compared with Au/SiO$_2$, and thus the lower sublimation energies found for the clusters may arise because of the preferential evaporation of Au at the periphery of the clusters. In any case, this contrast of

Fig. 10 The activity for CO conversion as a function of reaction time at 300 K on a model Au/TiO$_2$(001) catalyst. The initial average Au cluster size was 2.4 nm.

![Graph showing the activity for CO conversion.](image)

Fig. 9a shows a family of TPD spectra taken of the Au clusters deposited onto a SiO$_2$ thin film. The leading edge of the TPD peak maxima shifts to higher temperatures as the Au coverage increases. The inset shows a plot of the sublimation energy ($E_{sub}$) as a function of Au coverage, determined using the leading edge analysis.$^{[57]}$ At 0.2 ML, the $E_{sub}$ at $\sim 50$ kcal mol$^{-1}$ increases rapidly (with increasing Au coverage) to the bulk value at $\sim 90$ kcal mol$^{-1}$ at 5.0 ML. The decrease in $E_{sub}$ can be explained by the fact that an atom at the edge of a small cluster has fewer nearest neighbors than larger ones and hence desorbs more easily because of decreased surface tension.

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Fig. 11 A 50 $\times$ 50 nm$^2$ image of the same area taken at 450 K: (a) under ultrahigh vacuum conditions; (b) during exposure to a reaction mixture consisting of a 665 Pa CO:O$_2$ mixture. (View this art in color at www.dekker.com.)

![Image of surface regrowth around Au clusters, cluster size increase, cluster size reduction, and adhesion of cluster to tip.](image)
behavior regarding the sublimation of Au from SiO$_2$ and TiO$_2$ highlights the role of the support in altering the properties of ultrasmall clusters of Au.

Catalyst Deactivation and Cluster Sintering

The presence of reactant gases at realistic conditions can affect the admetal’s ability to wet the surface and thereby alter particle size and distribution. For example, although the TiO$_2$-supported Au catalysts exhibit a high activity for the low-temperature CO oxidation, the catalysts are often rapidly deactivated.$^{[46]}$ This is illustrated by Fig. 10, where the CO conversion is plotted as a function of reaction time for CO oxidation at 300 K on a catalyst prepared by depositing 0.25 ML Au on TiO$_2$. The model Au/TiO$_2$ catalyst, which exhibits a high initial activity, deactivates after a CO:O$_2$ (1:5) reaction of $\sim$120 min at 40 Torr. The deactivation is a result of the agglomeration of the Au clusters induced by interaction of O$_2$ with the Au clusters.$^{[58,59]}$

In Fig. 11, a selected area is shown in (a) for UHV conditions and in (b) for 665 Pa of a CO:O$_2$ (1:5) reaction mixture.$^{[59]}$ There are noteworthy parallels between the instability of the small Au clusters, their catalytic activity, and the change in their catalytic activity with time. Au clusters of approximately 3 nm are optimum as CO oxidation catalysts. Clearly, reaction-induced sintering of these small clusters is a mechanism for the loss of activity with time.

CONCLUSION

Model catalyst systems combined with surface-sensitive methods constitute a valuable methodology for probing the electronic and morphological structure of supported metal clusters. From detailed STM/STS studies combined with other surface analytical techniques, a physical basis for understanding the enhanced catalytic activities of nanosized, dispersed metal clusters is developing. The results summarized in this article show a close correlation among cluster size, morphology, electronic properties, and catalytic activity. The use of model catalysts prepared with metal clusters supported on thin oxide films has been essential for the development of these new insights into the special electronic and chemical properties that govern the unique catalytic chemistry of nanosized metal clusters. Future studies toward a more in-depth understanding of nanostructured supported clusters will undoubtedly lead to the design and the development of practical catalysts.

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