The Influence of Metal Cluster Size on Adsorption Energies: CO Adsorbed on Au Clusters Supported on TiO₂

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Abstract: Infrared reflection absorption spectroscopy (IRAS) has been used to study CO adsorption on Au clusters ranging in size from 1.8 to 3.1 nm, supported on TiO₂. The adsorbed CO vibrational frequency blue-shifts slightly (approximately 4 cm⁻¹) compared to that adsorbed on bulk Au, whereas the heats of adsorption (ΔH_ads) increase sharply with decreasing cluster size, from 12.5 to 18.3 kcal/mol.

Introduction

Following the discovery that small Au clusters supported on reducible metal oxides are effective catalysts for CO oxidation at room temperature, the partial oxidation of alkenes, hydrogenation, and nitrogen oxide reduction (ref 1 and references therein), numerous studies of Au and supported Au systems, particularly focused upon CO oxidation, have been undertaken in an effort to elucidate the origins of this unexpected and potentially useful phenomenon. A CO oxidation process that is efficient at low temperatures has several applications, including the elimination of CO from automobile emissions, hydrogen gas (for fuel cell applications), and CO₂ lasers. The potential for a single-step, direct process for the production of propylene oxide from propylene would greatly simplify production and reduce the cost of this very important chemical feedstock.

Many Au catalyst studies have focused on high surface area powdered catalysts (~60–90 m²/g) used under the elevated pressure and temperature conditions common to industrial applications. These “real-world” catalysts typically are synthesized via deposition—precipitation of HAuCl₄ onto powdered TiO₂ supports followed by calcining in air at 673 K. TEM results have shown that this procedure forms hemispherical Au clusters in the range of 3.5 ± 0.8 nm in diameter, a size regime found to promote CO oxidation at 293 K and below without significant deactivation. For CO pressures above 13.0 Torr and O₂ pressures above 6.5 Torr, the process was shown to be zero order in both reactants and, furthermore, exhibited little temperature dependence. It was also found that while the clean TiO₂ support material is not an active CO oxidation catalyst, unsupported Au clusters substantially larger than the TiO₂-supported Au clusters referred to above can catalyze the reaction between oxygen and CO, albeit at a rate 2 orders of magnitude lower than the Au/TiO₂ system. This finding contrasts with CO oxidation studies over a single-crystal Au(110) sample, where it was found that while the reaction does indeed have a very low activation energy (2 kcal/mol), oxygen dissociation must be facilitated by hot filament ionization, for example, since bulk Au does not thermally activate oxygen. These results suggest that the Au cluster size, the support material, or both, are critical to determining catalytic activity.

A study by Grunwaldt et al. investigated Au clusters on various supports in an effort to determine whether Au possesses intrinsic catalytic properties or whether the support plays a substantial role. Studies comparing Au colloids supported on TiO₂ and on ZrO₂ were carried out, including high-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), thermal desorption experiments, reaction studies, surface area determinations, and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). It was found that while the samples were similar as prepared, significantly more cluster sintering occurred on ZrO₂ under oxidizing pretreatment and reaction conditions. As the treatment temperature was increased, the CO oxidation rate reached a maximum and then decreased as a result of Au cluster sintering. Furthermore, the activity of the Au/TiO₂ surpassed that of the Au/ZrO₂ for equivalent reaction conditions. DRIFTS measurements confirmed that the CO stretching frequency exhibited a larger blue-shift under reaction conditions on the Au/TiO₂ than on Au/ZrO₂. Finally, XPS results showed that regardless of the support, the Au clusters were in the metallic state. These results suggest a substantial support role in the catalytic activation of Au. In support of this hypothesis,
Schubert et al.\textsuperscript{13} have recently proposed that a substrate’s ability to activate oxygen through a mobile superoxide intermediate is critical to the catalytic activity of supported Au. These authors concluded that cluster size is only a factor in determining catalytic activity when Au is supported on a substrate that does not activate oxygen.

Universal conclusions are difficult to draw from these high surface area catalyst studies due to the numerous differences between samples, studies, and preparations. On titania alone, Au has been deposited via deposition–precipitation,\textsuperscript{7, 10–14} impregnation,\textsuperscript{13, 14} impregnation of titanium hydroxide followed by calcination in air,\textsuperscript{3} and application of colloids.\textsuperscript{12, 15} While most studies report active catalysts that are pretreated by calcining in oxygen or air, Bollinger et al.\textsuperscript{14} showed that impregnated catalysts must in fact undergo hydrogen reduction at 773 K for highest activity and are deactivated by calcination. Guided strictly by DRIFTS measurements, some researchers have concluded that the oxidation state of adsorbed Au is positive,\textsuperscript{2, 12} while others have hypothesized that electron transfer from surface F-centers (electrons trapped in surface defects) results in negatively charged Au clusters.\textsuperscript{10}

Model Au/TiO$_2$ catalysts coupled with modern surface probes have addressed important issues with respect to the catalytic activity of highly dispersed Au clusters. Bollinger and Vannice\textsuperscript{14} employed the novel approach of depositing titania onto macroscopic (10 $\mu$m) Au clusters in an effort to distinguish between the interface region effects and those attributed to cluster size. Valden et al.\textsuperscript{16–19} have performed a series of scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), and CO oxidation kinetics studies of Au vapor-deposited onto a TiO$_2$(110) single crystal and a TiO$_2$(001) thin film. Catalytic activity was found to be a function of the Au cluster size; furthermore, maximum catalytic activity for these clusters was found to coincide with the metal-to-nonmetal transition occurring in clusters approximately 3.0 nm in diameter, as determined by STS cluster band gap measurements. This cluster diameter also coincides with a cluster growth transition from the nucleation of flat, two-dimensional clusters to their agglomeration into hemispherical, three-dimensional structures, as measured by STM.

In a second study, CO adsorption and oxidation were monitored on TiO$_2$-coated Au(111)/mica films,\textsuperscript{15} where virtually no adsorption and no catalytic activity were observed. In a study of the model Au/TiO$_2$(110) system, oxygen was reported to bind more tightly on single or double atomic layer Au clusters than on multilayer ones,\textsuperscript{20} another indication of morphology-dependent chemistry. Recent temperature-programmed desorption (TPD) studies by Shaikhudinov et al.\textsuperscript{21} have measured CO adsorption on Au clusters in a range of sizes on substrates associated with catalytically active (FeO$_x$, FeO), and inactive (Al$_2$O$_3$) systems. These studies found that regardless of substrate, gold particles of a threshold diameter (3.0 nm) desorb CO at the same maximum temperature (170 K). In summary, evidence obtained from model catalyst studies suggests a combined chemical effect of cluster morphology and electronic structure.

The present studies assess the chemisorption and binding energies of CO on Au clusters supported on titania, using infrared reflection absorption spectroscopy (IRAS). IRAS affords exceptional advantages toward understanding the chemical and physical properties of supported metals.\textsuperscript{22–24} More importantly, because IRAS is a photon-in/photon-out technique, it is amenable to studies at elevated reactant temperatures and pressures. IRAS is thus suitable for use in both UHV and elevated pressure environments and therefore can be used in situ, providing a bridge between data collected from idealized models and DRIFTS data collected from more realistic catalytic systems over a range of pressures from UHV to ambient. Studies\textsuperscript{25, 26} have shown that IRAS can be used quite effectively to bridge the so-called “pressure gap.”

Most high surface area vibrational studies report that CO weakly adsorbs on titania (2206–2170 and 2115 cm$^{-1}$) and forms more stable surface carbonates, bicarbonates, and formates (many features from 1854 to 1222 cm$^{-1}$), depending upon the degree of surface hydroxylation and/or water coadsorption.\textsuperscript{7, 14–20} While it has been proposed that these may act as intermediates in catalytic processes, isotopic scrambling studies have largely discounted that possibility by showing that the original C–O bond does not dissociate at any point in the oxidation process.\textsuperscript{21, 22} Observations of the interaction of CO with TiO$_2$ single crystals tended to confirm the results obtained on powdered materials. Infrared spectra collected from CO adsorbed on a vicinal cut TiO$_2$(770) single crystal measured vibrational frequencies similar to the aforementioned (2174, 2150, and 2133 cm$^{-1}$) and low adsorption energies (between 4.9 and 6.6 kcal/mol).\textsuperscript{23} Studies of CO adsorption on rutile TiO$_2$(110) confirmed weak adsorption (9.9 kcal/mol); they also revealed that while the CO heat of adsorption increases with an increase in surface oxygen vacancies, there was no significant concomitant effect on the number of CO molecules adsorbed on a given sample.\textsuperscript{24} Recent ab initio calculations of CO bound to Ti$^{4+}$ through the carbon atom yielded solutions in good agreement with the experimental results.\textsuperscript{25, 26}

The synthesis of TiO$_2$ thin film on refractory metal substrates and their subsequent characterization is well-established. Depending upon the substrate crystal face used and the film growth procedure, it is possible to produce TiO$_2$(001)/Mo(100),\textsuperscript{27} TiO$_2$(100)/Mo(110), Ti$_2$O$_3$(0001)/Mo(110), TiO$_2$(0001)/Mo(110),\textsuperscript{30} or TiO$_2$(110)/Mo(110).\textsuperscript{36} These films have been used quite successfully in the
study of model-supported Au catalysts. Ion scattering spectroscopy (ISS), TPD, STM, STS, and reaction kinetics studies have been used quite successfully to monitor the change in cluster morphology as a function of temperature as well as the catalytic activity and electronic structure as a function of cluster size using these thin film models as substrates. Due to the reflective surface requirements of IRAS, thin-film metal oxide model supports on refractory metal substrates are most suitable for its use. In the present study, thin TiO$_2$ films supporting a range of Au coverages were produced and studied under CO adsorption conditions.

**Experimental Section**

This study was performed in a UHV chamber equipped with a Perkin-Elmer Auger electron (AES) spectrometer, a UTI Instruments quadrupole mass analyzer, a Physical Electronics low-energy electron diffraction (LEED) spectrometer, a Perkin-Elmer ion sputtering gun, and an infrared cell separated from the main chamber by a sliding seal. This apparatus has been described in detail elsewhere. The infrared cell was fitted with flange-mounted CaF$_2$ windows in the infrared beam path. In the infrared cell, the sample could be pressed independently of the main UHV chamber, thus allowing experiments to be performed at elevated pressures without affecting the main chamber vacuum. Pressure in both the main chamber and in the infrared cell was measured using a Granville-Phillips ionization gauge.

A Mattson Cygnus 100 infrared spectrometer equipped with a liquid nitrogen-cooled MCT detector was used in single-beam mode to collect the IRAS spectra. All IRAS spectra collected in this study were averages of 512 scans at 4 cm$^{-1}$ resolution, requiring 4.5 min collection time. The spectra of CO adsorbed on the TiO$_2$ and Au/TiO$_2$ substrates were acquired as the inverse log of the single background emissivities at the recorded temperatures and CO pressures divided by the emissivities recorded at 450 K and at 10$^{-5}$ Torr background pressure. It was found that this step was necessary to avoid alteration of the reference spectra by measurable CO absorbance from adsorption of the background gas.

The sample was a Mo(110) single crystal (Single-Crystal Limited) mounted on the sample probe with a tantalum wire loop spot-welded around the edge of the sample and a type C thermocouple spot-welded to the back. The type C thermocouple (W-5%Re/W-26%Re, wire provided by H. Cross Co.) was used because its rhenium/tungsten alloys are high melting and exhibited a well-characterized potential vs temperature profile. This mount allowed for resistive heating to 1200 K and liquid nitrogen cooling to ~80 K. The sample was cleaned by alternating annealing at 800 K in 5 x 10$^{-4}$ Torr O$_2$ (99.999%) and electron beam heating to 2000 K until no carbon or oxygen was observed using AES. The Ti doser was constructed by wrapping titanium wire (99.999%, Goodfellow) around a tungsten wire loop (H. Cross) that could be heated resistively. The doser was outgassed thoroughly by resistive heating prior to use. Oxygen and carbon monoxide (99.999%, Matheson Gas Products) were further purified by fractional condensation and transferred to glass bulbs. The CO bulb was immersed in liquid nitrogen during the experiments to condense volatile metal carbyls that are typically formed when the steel gas manifold is exposed to CO.

The TiO$_2$ thin films (4 MLE TiO$_2$, calibrated by Auger break point) were produced by evaporation of titanium metal onto the Mo(110) crystal at 650 K in a background of 5 x 10$^{-5}$ Torr O$_2$. The films were annealed to 800 K in this oxygen background to ensure full oxidation and to eliminate adventitious carbon occasionally found in the films prior to annealing. Details of the film synthesis and characterization can be found elsewhere; essentially, these films were the rutile phase with a preponderance of (110) facets. This particular film was chosen for its high thermodynamic stability and for its morphological similarity to the TiO$_2$(110) single crystal already extensively studied using STM, IRAS and TPD of CO were performed at pressures up to 10 Torr and temperatures as low as 80 K before cooling loss due to gas convection warmed the sample to over 200 K. No significant absorption was found by TPD or IRAS on the titania film at 80 K; no carbonate or physisorbed species reported for high surface area samples or implied by previous theoretical studies were observed. The extremely low concentration of adsorbed CO indicated a surface largely free of oxygen defect sites, which were thought responsible for CO bonding.

Following these experiments, Au was applied to the surface via vapor deposition. The Au dosing rate was calibrated via both Auger break point analysis and TPD. The Au source was a resistively heated tungsten filament tightly wrapped with high-purity Au wire (99.9999%, Goodfellow). The Au evaporator was thoroughly outgassed by resistive heating prior to use. After Au was applied, the samples were annealed to 450 K in a vacuum for 10 min prior to CO IRAS experiments. This step was taken to agglomerate the Au clusters in concordance with the plateau observed in the ISS thermal stability curve. Reference spectra were collected before and after each series of isotherms to ensure that the clusters were thermally stable during the experiments. If a significant deviation was observed in either the vibrational frequency or total absorbance intensity, the sample was resistively heated to 1000 K with a relatively slow heating rate (maximum of 2 K/s), held at that temperature for two minutes, and then cooled. This procedure was repeated until no Au was visible by AES, after which the procedure was repeated. At this point, the titania film was deemed suitable for deposition of new Au clusters. Even though these annealing cycles were performed in such a way as to avoid disruption of the titania film, after several cleanings, the molybdenum substrate became increasingly more evident in AES, suggesting film damage that required growth of a new titania film. Damaged films were removed by e-beam heating to 2000 K.

**Results and Discussion**

Figure 1 shows an IRAS spectrum of CO adsorbed on 4 MLE Au/TiO$_2$. This coverage was chosen to provide a benchmark where CO adsorption behavior is expected to approach that of metallic Au systems. The peak vibrational frequency at 2122 cm$^{-1}$ contrasts with the value of 2108 cm$^{-1}$ observed for large CO coverages on Au(110) - (1 × 2), 42,43 2115 cm$^{-1}$ on gold films, and 2110 cm$^{-1}$ on Au(110). This small blue-shift in the CO frequency of titania-supported Au compared to a variety of bulk gold samples indicates the possibility of a substrate effect. While this blue-shift may be due to the large percentage of low-coordination Au atoms expected for Au clusters, it is notable that the reconstructed Au surface contains a substantial percentage of six-coordinate Au atoms. For this reason, substrate effects appear to be the most likely cause of this shift. This conclusion is further supported by IRAS of CO/Au/Al$_2$O$_3$, Au supported on a nonreducible metal oxide. The frequencies measured for this system range from 2101 to 2111 cm$^{-1}$, slightly lower than those observed for Au/TiO$_2$. This difference is likely due to the different nature of the substrate, with TiO$_2$ providing stronger electron donation compared to Al$_2$O$_3$.

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lower than the corresponding bulk Au frequencies. Different Au cluster substrates indeed have subtle effects on the adsorbed CO vibrational frequency. Furthermore, only a single feature is evident; no secondary feature related to a chemically distinct interface site is apparent, nor are any other features that have been previously attributed to CO bound to TiO$_2$.

Figure 2 shows IRAS data collected at 190 K for CO adsorbed on 0.5 MLE Au/TiO$_2$, the Au coverage expected to form clusters with a mean diameter for which a metal-to-nonmetal transition is observed.$^{19}$ The frequency at lowest coverage is 2126 cm$^{-1}$ and shifts to 2122 cm$^{-1}$ as the pressure is increased. Only a single feature is evident, suggesting only a single adsorption site, similar to that found for bulk Au. A significantly reduced absorption intensity is observed, since there are significantly fewer CO molecules adsorbed on the Au clusters compared to a single crystal (the Au surface area available for adsorption is much smaller). The isotherms (Figure 3) resemble the Langmuir isotherm, suggesting relatively weak dipole–dipole interadsorbate interactions between adsorbed CO molecules (a primary source of adsorbate depolarization and thus infrared signal attenuation) consistent with CO adsorption on small clusters spaced some distance from each other. This contrasts with the IRAS intensity attenuation caused in part by CO depolarization observed on bulk metal surfaces at high coverage.$^{47}$ The Langmuir isotherm fits somewhat poorly to the data at the high and low coverage extremes. This result suggests that the adsorption equilibrium constant varies with coverage, which is expected from systems wherein the heat of adsorption is not constant with respect to coverage.

From the slopes of the isosteric plots (Figure 4), heats of CO adsorption as a function of coverage can be derived (Figure 5). For these data, saturation of the IRAS signal is assumed to be approximately 100% coverage due to the nearly perfect Langmuirian behavior of the isotherms. It is noteworthy that at the zero coverage limit, the heat of adsorption ($\sim$12.5 kcal/mol) is only slightly higher than that measured for bulk Au–TiO$_2$–(110)–(1 $\times$ 2) using the Clausius–Clapeyron method applied to isosteres of IRAS data ($10.9$ kcal/mol)$^{43}$ and less than that measured using the same method to determine the heat of CO adsorption on bulk gold films (13.4 kcal/mol)$^{44}$ as well as isosteric heats derived from work function measurements on Au–TiO$_2$–(1 $\times$ 2) (14.1 kcal/mol).$^{48}$ The one anomaly between the behavior of the supported and bulk Au is the percentage of the saturation coverage of CO that binds at a particular energy. For bulk Au, the heat of adsorption falls to 8.3 kcal/mol at

![Figure 1](image1.png)

Figure 1. IRAS of CO/4 MLE Au/TiO$_2$. $P_{CO} = 10^{-3}$ Torr, $T = 205$ K. Note blue-shift with respect to CO on bulk Au at saturation.

![Figure 2](image2.png)

Figure 2. IRAS spectra of CO/0.5 MLE Au/TiO$_2$ collected at 190 K. Note minor deviation from 4 MLE frequency.

![Figure 3](image3.png)

Figure 3. IRAS isotherms of CO/0.5 MLE Au/TiO$_2$. Due to resemblance to the Langmuir isotherm, interadsorbate vibrational interaction is assumed to be minimal, and thus, maximum integrated intensity is assumed to approximate 100% CO coverage. Traces are included to guide the eye and aid in interpolation of isosteres.
approximately 19% CO coverage; for the supported cluster, the zero coverage heat of adsorption is sustained to approximately 33% of the saturation coverage. While Au clusters in this size regime may not directly activate CO for oxidation, they might influence the reaction by increasing the surface concentration of CO relative to bulk Au.

At 0.25 MLE Au/TiO₂, changes become evident in the heat of adsorption of CO, but not in the vibrational characteristics. Figure 6 shows CO adsorbed on these Au clusters at 220 K; note the lack of significant differences between these spectra and those for larger Au clusters. The vibrational frequency is 2123 cm⁻¹ throughout the entire CO coverage range. The isotherms (Figure 7) no longer exhibit Langmuirian behavior, nor can CO coverage be approximated from a point of diminishing intensity caused by dipole–dipole interactions (small, distant clusters are not expected to provide a sufficient number of neighboring adsorbed oscillators). As a result, the CO coverage for this model system and for 0.125 MLE Au/TiO₂ (which suffers the same limitation) will be reported as relative coverages that are a function of integrated peak intensity. No linearity is implied using this method (in the event that this deviation from Langmuirian behavior belies a coincident deviation from strict Beer–Lambert behavior); only qualitative relative coverage is claimed. With this in mind, the slopes of the isosteric plots (Figure 8) and the resulting heats of adsorption with respect to integrated intensity (Figure 9) are shown. Immediately evident is the significant increase in \(-\Delta H_{\text{ads}}\) to
18.2 kcal/mol. Even at the highest measured coverage, the heat of adsorption of 14.5 kcal/mol exceeds that of the zero-coverage limit for bulk Au and for 0.5 MLE Au/TiO₂. These higher heats of adsorption are maintained as Au coverage decreases further to 0.125 MLE. Shown are representative spectra collected at 220 K (Figure 10), the isotherms from this sample cluster size (Figure 11), and the isosteric heats of adsorption (Figure 12). The zero coverage value of \(-\Delta H_{\text{ads}}\) is approximately 16.3 kcal/mol and maintains that level for the entire measured coverage range.

As Au coverage (and therefore cluster size) decreases, greater percentages of adsorbed CO (with respect to maximum integrated IRAS intensity) are activated at or near the zero-coverage energy limit. On a given gold cluster, any bound CO molecules could very likely have a chemical effect on the adsorption of the next CO molecule to the same cluster, leading to changes in heats of adsorption with increasing coverage. Smaller Au clusters should allow fewer CO molecules to adsorb at saturation compared to larger clusters. In the limit of isolated Au clusters one atom in size, each cluster should adsorb one CO molecule. Provided there is sufficient separation between clusters (to reduce interadsorbate interactions) on an insulating substrate (to prevent intercluster electronic interactions), CO adsorbed on any cluster should exhibit the same vibrational frequency and heat of absorption regardless of the CO surface coverage of available cluster sites. The small decrease in the heat of adsorption with CO coverage suggests that 0.125 MLE Au/TiO₂ is very near this limit. Alternatively, it can be argued that the widening band gap present in clusters of this size regime is preventing interadsorbate interactions through the substrate, leaving only dipole–dipole interactions to deviate the observed isotherm behavior from Langmuirian behavior observed on the larger metallic clusters.

The trend observed in these results compare well to similar values found using the Redhead approximation⁴⁹ to analyze CO adsorption on Au clusters supported on TiO₂.
TPD from Au clusters adsorbed to Fe₂O₃, FeO, Al₂O₃, and TiO₂ all of these studies using surface science models agree that 30 Å Au clusters activate CO at higher heats of adsorption than bulk gold systems. The Au coverages applied in this study are converted to average cluster sizes as measured by STM; this approximation is validated by the equivalent materials and methods employed in sample production in both studies. These are plotted (Figure 13) alongside CO/Au/TiO₂ TPD data. Both methods show a trend toward higher heats of adsorption at the lower cluster size limit. The results derived using the Clausius–Clapeyron relation actually show a much sharper transition from bulk adsorption properties to cluster adsorption properties than do the values derived using the Redhead method. The maximum $-\Delta H_{\text{ads}}$ occurs at approximately the same cluster size for which a metal-to-nonmetal transition and maximum in catalytic activity were found by Valden et al. The sharp change in catalytic activity as well as in CO heat of adsorption belies the narrow particle size distribution in both systems and bolsters the assertion that the samples from both studies are equivalent.

The insensitivity of the CO frequency to cluster size is noteworthy. It appears that neither cluster size nor an interface region have a significant effect on the vibrational energy of bound CO, although a very slight overall blue-shift with respect to bulk Au is evident in all supported Au samples in this study. Interpretation of this shift is complex; increases in σ bonding (blue-shift) and/or π back-donation (red-shift), polarization changes in the cluster and the molecule, tilting of the CO molecule, and changes in the “wall effect” (electrostatic repulsion of Au and CO overlapping electron orbitals) could all change the frequency by a few wavenumbers. It is likely that a combination of these is operative, some reinforcing and some compensating. For example, increasing the σ bonding results in a slight blue-shift (and stronger adsorption); however, doing so also reduces the amount of electron density that experiences steric repulsion from the Au 5d orbitals, reducing the wall effect, thereby causing a red-shift. Increasing the π back-donation into antibonding CO orbitals, on the other hand, would also be consistent with greater heats of adsorption, but would cause a red-shift in vibrational energy. Since stronger bonds tend to have shorter equilibrium bond distances, an increase in the wall repulsion may compensate this red-shift by increasing the orbital overlap as the CO molecule moves closer to the Au atom. Electron transfer via back-donation would also tend to decrease the C–O bond order (formally between 2 and 3) toward that of CO₂ (formally 2), a favorable development for promoting catalytic oxidation of CO.

Conclusions

In this study, the isosteric heats of adsorption ($-\Delta H_{\text{ads}}$) are reported for a series of Au clusters on titania covering the size

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(54) Bagus, P. S.; Texas A&M University, Department of Chemistry, Personal communication, 2001.
range within which a metal-to-nonmetal transition and a maximum of oxidative catalytic activity have been previously observed.\textsuperscript{19} While clusters corresponding to 0.5 MLE Au coverage behave largely as the bulk metal, reducing the metal coverage (and the corresponding cluster size) substantially increases the $-\Delta H_{\text{ads}}$ for CO, from $\sim$11 kcal/mol to $>18$ kcal/mol, roughly 60%. The Au cluster size corresponding to the highest $-\Delta H_{\text{ads}}$ for CO is very close to that exhibiting the maximum catalytic activity for CO oxidation. Therefore, within experimental error, the metal-to-nonmetal transition, the increase in CO heat of adsorption, and the onset of catalytic oxidation occur concomitantly with respect to cluster size. In a related study,\textsuperscript{20} Au/TiO$_2$ systems with clusters in this size regime have also been observed to bind atomic oxygen more strongly than systems with larger gold clusters. Clearly, the enhanced binding of CO and oxygen for nanosized clusters are central to understanding the enhanced catalytic properties for Au clusters supported on TiO$_2$ compared to bulk Au. The heats of adsorption of CO on transition metals are typically much higher (Pt,\textsuperscript{55} Pd,\textsuperscript{56,57} and Rh\textsuperscript{58}) or much lower (macroscopic Au,\textsuperscript{43,44,48} Cu\textsuperscript{59}) than those measured for the more catalytically active gold clusters examined in the present study. Excessive high binding of CO precludes CO oxidation at temperatures well below the CO desorption temperature, e.g., room temperature, since CO prevents oxygen adsorption. On the other hand, a higher binding energy of CO than that exhibited by bulk Au is necessary to provide sufficient concentrations of CO on the surface for reaction to occur. Apparently, the enhanced binding of CO on Au nanoclusters relative to bulk Au is near optimum for promotion of CO oxidation at room temperature.

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