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Structure–activity relationships in supported Au catalysts

M.S. Chen, D.W. Goodman [*]

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

Abstract

Au-based catalysts have great potential because of their unique activity and selectivity for a variety of important reactions. The special catalytic properties of supported Au nano-particles depend critically upon the particle morphology, i.e. size, shape and thickness, as well as support effects. This paper reviews the current understanding of CO oxidation on supported Au catalysts. The electronic structure of Au particles at various nucleation sites and on different supports is summarized, and the effect these changes have on catalytic performance is discussed. Recent results from our laboratories have demonstrated the synthesis of well-ordered Au mono- and bi-layer films on a titanium oxide support and show that the active Au structure for CO oxidation is an electron-rich, Au bi-layer. In contrast, the monolayer structure, which may involve the TiO_x support, is significantly less active (by less than an order of magnitude) than the Au bi-layer. The oxidation state of the Au and how this relates to the catalytic activity are also discussed.

Keywords: Au catalyst; Nano-particles; Electron-rich

1. Introduction

Au has long been considered catalytically less active than other transition metals. However, highly dispersed Au has received considerable recent attention because of its extraordinary catalytic properties [1–10] first demonstrated by Haruta [1]. Au particles of less than 5 nm diameter have been found to be active for low temperature CO oxidation [1], propylene epoxidation [11–14], water gas shift reaction [15–19], NO reduction/dissociation [20,21], hydrogenation [22,23], SO_2 dissociation [24] and selective oxidation [25,26].

Of the important reactions known to be catalyzed by supported Au particles, the low temperature CO oxidation has been received the most attention experimentally and theoretically [1–7,27–34]. However, the data in the literature vary widely, and the nature of the active Au species/structure/site remains obscure. It is generally accepted that the catalytic activity of Au depends to a large extent on the size of the Au particles, however other effects, such as the nature of the support material, the Au-support interface, the particle shape, and metal–support charge transfer, are purported to be of fundamental importance. In this article, recent progress with respect to CO oxidation on Au-based catalysts is summarized, and the current understanding of the active site and the reaction mechanism are reviewed.

2. Particle morphology

The low-temperature oxidation of CO on supported Au particles shows a marked increase in the turnover frequency (TOF, reaction rate per surface Au site per second) as the diameter of the Au particles is reduced below ~3.5 nm [35,36] (Fig. 1). A further reduction in the particle diameter below ~3 nm leads to a decrease in the catalytic activity. Despite the extensive recent efforts to address this unusual catalytic behavior of ultra-small Au particles, no atomic-level understanding currently exists.

Upon exposure of a Au/TiO_2 model catalyst to realistic reaction conditions, data similar to those displayed in Fig. 1 have been acquired for CO oxidation activity as a function of Au particle size (Fig. 2) [27,37]. The apparent activation energy for the reaction between 350 and 450 K varies from 1.7 to 5 kcal/mol as the Au particle size is increased from 2.5 to 6.0 nm. Model catalysts provide a well-defined catalytic surface which, when combined with surface analytical techniques, can directly probe structure/function relationships.

In these studies [27,37], Au was deposited onto a TiO_2 surface at 300 K with a subsequent anneal at 850 K for 2 min

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

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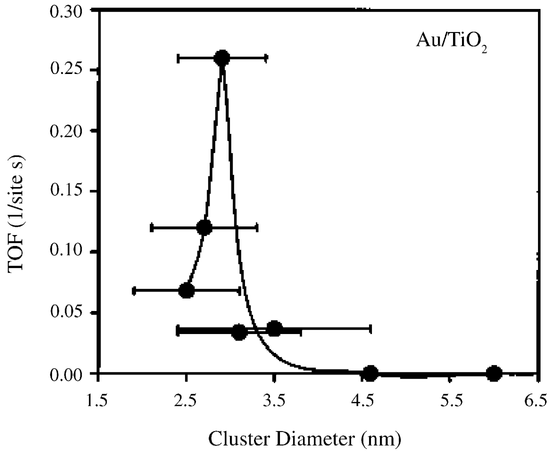

Fig. 1. CO oxidation turnover frequencies (TOF's) at 300 K as a function of the average size of the Au particles supported on a high surface area TiO_2 support [36]. The Au/TiO_2 catalysts were prepared by deposition–precipitation method, and the average particle diameters were measured by TEM. The solid line serves merely to guide the eye. [35,36].

[38]. By varying the initial Au coverage, Au particles from 1 to 50 nm can be synthesized with relatively narrow particle size distributions. A typical STM image of 0.25 monolayers (ML) Au on TiO_2(1 1 0)-(1 × 1) is shown in Fig. 2. The Au particles are imaged as bright protrusions with an average size of ~2.6 nm in diameter and ~0.7 nm in height (two to three atomic layers). The structure and related chemistry of TiO_2 has been reviewed in detail by Diebold [39]. The growth of Au on the TiO_2(1 1 0) surface at 150–300 K has also been examined using X-ray photon spectroscopy (XPS) and low energy ion scattering (LEIS) by the Campbell [40] and Madey [41] groups. Two-dimensional (2-D) Au islands are initially formed up to a certain critical coverage which decreases with temperature and increases with the defect density of the TiO_2 surface, as shown in Fig. 3. Above this coverage, Au nucleates on top of the 2-D islands. 3-D islands are thermodynamically more stable, however, kinetic limitations constrain the growth initially to 2-D. This behavior has been explored using a kinetic model, which includes energies for Au atom migration [40,42].

To investigate the origin of the exceptional high activity for Au particles in the 3 nm size range, the tunneling current as a function of the bias voltage (*I*–*V*) for several Au particles of varying sizes supported on TiO_2(1 1 0)-(1 × 1) for various Au coverages from 0.2 to 4.0 ML was measured and is plotted in Fig. 2 as the band gap of the Au particle versus the particle size [27]. A metal-to-insulator transition occurs as the particle size falls below 3.5 nm in diameter and 1.0 nm in height (~300 atoms per particle). Particles that are only one atom thick have relative large band gaps, whereas particles with a thickness of three or more atomic layers exhibit metallic properties. The relative population of the Au particles with a band gap of 0.2–0.6 V, associated primarily with those Au particles with two atomic layer thickness, is shown in Fig. 2. The metal-to-insulator transition as a function of particle size, i.e. a quantum size effect, have also been observed for Pd/TiO_2(1 1 0) [38], for Ag particles grown in nano-pits on a graphite surface [44], and for Ag particles supported on Al_2O_3/NiAl(1 1 0) [45]. Recently, Haruta's group [46] has also inferred a similar metal–insulator transition for Au/TiO_2 by measuring the local barrier height (LBH) using STM. The LBH was found to be dependent on the

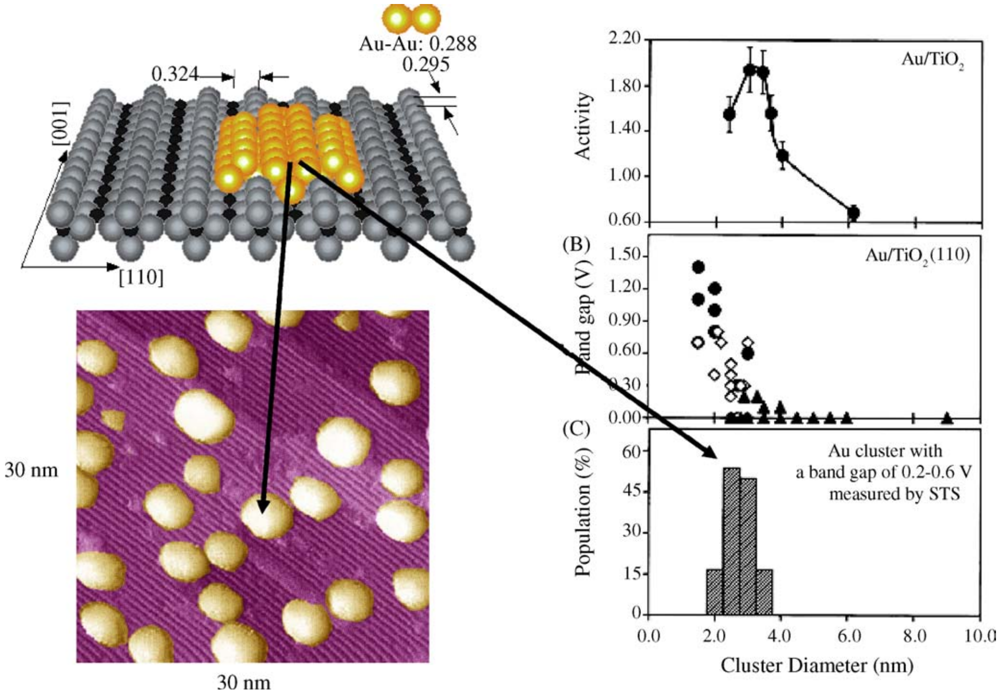

Fig. 2. A model structure of bilayer Au island on TiO_2(1 1 0) surface, and a STM image of Au/TiO_2(1 1 0)-(1 × 1) with Au coverage of 0.25 ML (left). The activity for CO oxidation at 350 K as a function of the Au particle size supported on TiO_2(1 1 0) assuming total dispersion of the Au. The CO:O_2 mixture was 1:5 at a total pressure of 40 Torr. Activity is expressed as (product molecules)/(total Au atoms) 1 s1; Particle band gap measured by STS as a function of the Au particle size; and relative population of the Au particles (two atom layers in height) that exhibited a band gap of 0.2–0.6 V as measured by STS from Au/TiO_2(1 1 0). [27,43].

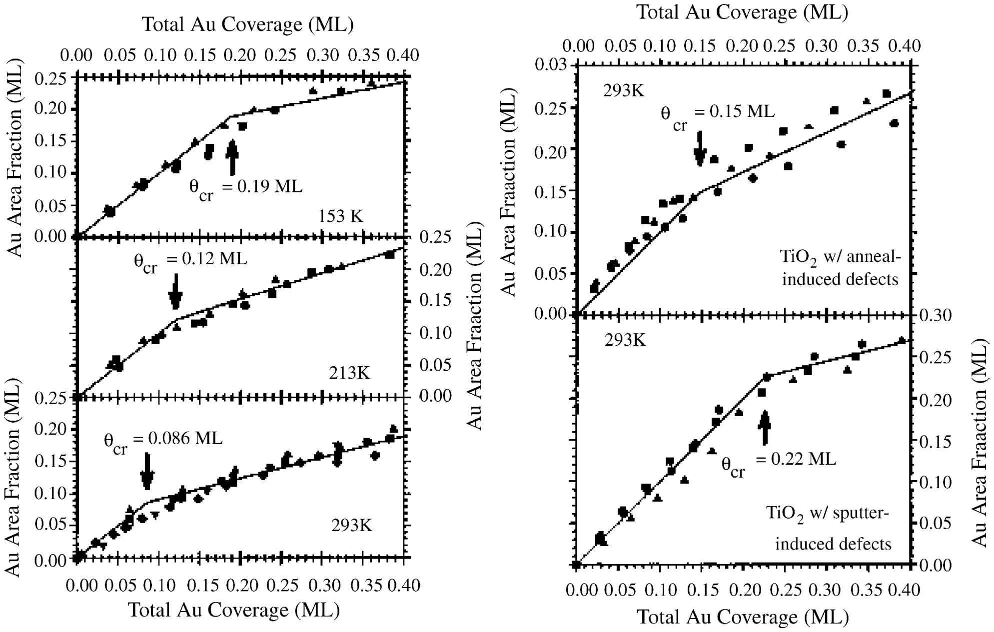

Fig. 3. The area fraction of Au islands on TiO_2(1 1 0) as a function of total Au coverage for Au deposition at ~0.3 ML min^{-1} at three different substrate temperatures: (a) 153; (b) 213; and (c) 293 K. Au growth on differently treated initial TiO_2 substrates at 293 K, followed by LEIS: (a) with anneal-induced defects; and (b) with Ar^+ sputtered defects. The anneal-induced defected surface was prepared by UHV anneals at 900 K, followed by a final anneal in 3×10^{-6} mbar O_2 for 10 min. The sputter-induced defected surface was prepared by annealing the surface in 3×10^{-6} mbar O_2 for 10 min, followed by a 30 s 1 keV Ar^+ sputter at 5×10^{-6} mbar Ar pressure to create defect sites on the surface. [40].

height of the Au particles in that the LBH of large particles ($>$0.4 nm in height) was approximately 0.3 eV larger than that of the substrate, whereas the LBH of small particles ($<$0.4 nm in height) was comparable to that of the substrate. The critical height of 0.4 nm for the LBH was proposed to correlate with the metal–insulator transition of the Au particles. On Au–FeO_x/SiO_2/Si(1 0 0) [47], the energy distribution of the photoelectrons from the 5d valence band of Au was found to depend markedly on the Au particle size, with the intrinsic catalytic activity of the Au particles increasing with decreasing particle size.

Infrared reflection absorption spectroscopy (IRAS) [48,49] was used to study CO adsorption on Au particles ranging in size from 1.8 to 3.1 nm, supported on TiO_2. The CO vibrational frequency on the Au particles blue-shifts slightly (approximately 4 cm^{-1}) compared to CO on bulk Au, whereas the heats of adsorption increase sharply with decreasing particle size, from 12.5 to 18.3 kcal/mol (Fig. 4). The maximum heat of adsorption occurred at approximately the same particle size where the catalytic activity maximizes and where a metal-to-insulator transition was observed by Valden et al. [27]. On Au/FeO(1 1 1)/Pt(1 1 1) surface [50], relatively small Au particles were shown to adsorb CO more strongly compared with large particles by temperature-programmed desorption (TPD) and IRAS. On small Au-particle anions (Au_n^-, $n = 4$–19), pulsed helium flow-reactor methods at room temperature showed a marked particle size dependency for CO adsorption [51].

Bilayer Au clearly has unique electronic (Fig. 5) [52] and chemical properties [48,53] from those of bulk Au. Furthermore, the population of two-atom-thick particles is peaked at particle diameters ranging from 2.5 to 3.0 nm, a size regime that correlates with the optimum particle size for catalytic activity in model and high-area Au/TiO_2 catalysts (Figs. 1 and 2). Based on these observations, it has been proposed [27] that the pronounced structure sensitivity of CO oxidation on Au/TiO_2 originates from quantum size effects with respect to the thickness of the Au particles. Those particles that exhibit a distinct band gap unlike that of a bulk metal are shown to be particularly suited for catalyzing the oxidation of CO.

Properties of the Au particles other than size have been suggested to give rise to the special reactivity of nano-sized Au,

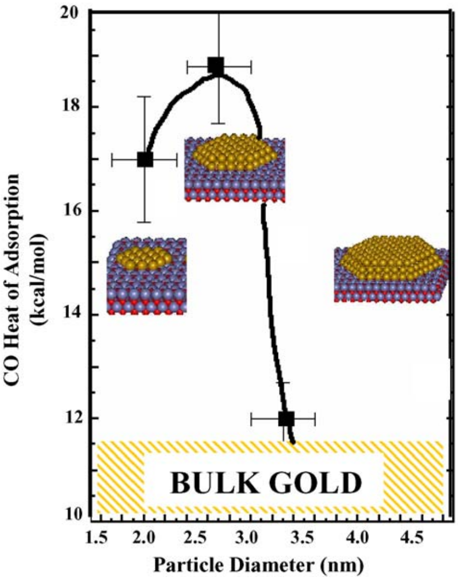

Fig. 4. Zero coverage isosteric heats of adsorption as a function of mean particle diameter [47], the value for Au(1 1 0)-(1 × 2) is shown for comparison [48].

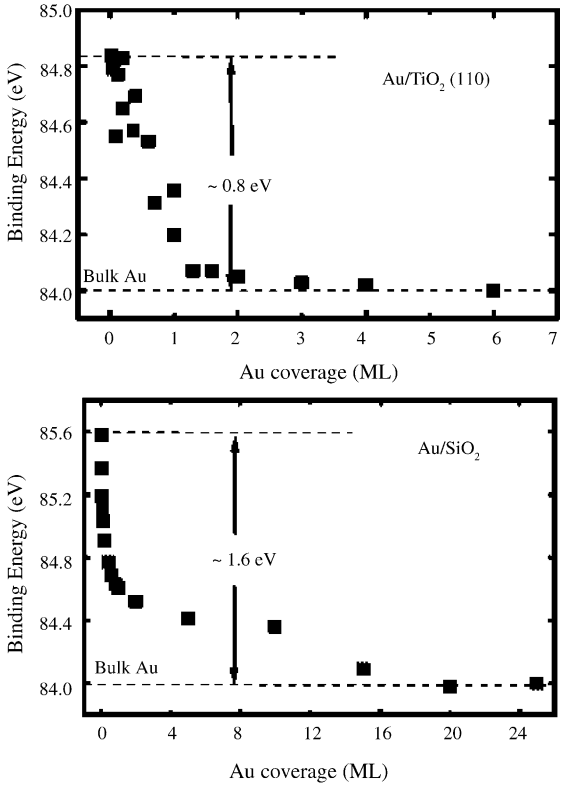

Fig. 5. Plots of XPS BE peak centers of the Au $4f_{7/2}$ core level as a function of Au particle coverage (ranging from 0.02 ML to bulk on TiO_2(1 1 0) and SiO_2 surfaces. [52].

namely uncoordinated edge atoms, and the Au particle–support interface [54–57]. These suggestions stem from experimental and theoretical results showing that CO or O_2 do not chemisorb on planar Au surfaces, but do chemisorb on stepped or rough Au surfaces [55–58]. On relatively small particles, the fraction of corner sites and low coordination atomic sites is higher than for relatively large particles, and thus small particles exhibit higher catalytic activity. The shape of the particle is then an important parameter in determining the fraction of the various types of surface Au atoms. The stronger bonding of O_2 on a rough Au surface compared with a planar Au surface [57,59,60] has been attributed to fact that in particles and on rough surfaces, the highest occupied molecular orbital (HOMO) is localized with its charge density projecting into the vacuum, facilitating charge transfer to the π^* orbital of O_2. This, in turn, enhances the bonding of O_2 to Au, in contrast to a planar Au surface that tends to delocalize the HOMO, diminishing the binding of the surface to O_2.

3. Support effects

Exceptionally high activities for oxidation of CO have been reported for highly dispersed Au on reducible oxides, e.g., TiO_2, Fe_2O_3, etc. [61–65]. Haruta et al. [61] emphasized the role of the perimeter interface between the Au particles and the support as a unique reaction site for the reactants adsorbed separately, one on Au and another on the support surfaces. To evaluate the role of the support [62], supported Au nanoparticles (Au/TiO_2, with a Au particle mean diameter of 3.5 nm) were compared with an unsupported Au powder (mean diameter of 76 nm) for CO oxidation. It was found that the Au/TiO_2 and the Au powder are active for CO oxidation at 253–293 K, but the rate constant of CO oxidation normalized to the Au surface area was larger by two orders of magnitude for Au/TiO_2 than for Au powder. Adsorption of CO occurred almost instantaneously and reversibly on pre-oxidized Au/TiO_2, whereas the Au powder showed no CO adsorption. During oxidation, O_2 in the gas phase may be directly activated on the Au particles and/or on the perimeter interface between the Au and the support. On a Au/FeO_x/SiO_2/Si(1 0 0) model system prepared by pulsed laser deposition (PLD) [47], it was found that the support or the perimeter of the Au particles play an important role in the catalytic activity of Au. Comparing the reactivity of Au particles (8–22 nm) supported on different metal oxides, e.g. TiO_2, ZnO, ZrO_2 and SiO_2, Au nanoparticles on TiO_2 was found to exhibit the highest activity compared to other supports for both CO oxidation and propylene hydrogenation [64].

Additional strong evidence for a support effect for Au/TiO_2 was provided by Overbury et al. [65]. By utilizing triamine ligand complexes and carefully controlling the preparation conditions, Au particles essentially identical in size (2–3 nm) were synthesized and supported on titania and on a wormhole silica. The results reveal that Au supported on titania exhibits a much higher activity for CO oxidation than for SiO_2. These results suggest that the presence of 2–3 nm size of particles alone is not sufficient to achieve high activity in CO oxidation. Instead, the support may influence the activity through other mechanisms including stabilization of sub-nanometer particles, formation of active oxygen-containing reactant intermediates (such as hydroxyls or O_2^-), or stabilization of optimal Au structures. It is noteworthy that Pietron et al. [66], have emphasized the importance of the Au-oxide contact area.

Several roles of the support in activating nanosized Au particles have been proposed including a source for nucleating sites and/or charge transfer, direct bonding to the reactants, and activation of the reactant. Defects on the support may markedly affect the adsorption energy and the electronic structure of a Au adlayer, and thus the catalytic properties of the supported Au particles. Numerous theoretical studies, many utilizing density-functional theory (DFT), have addressed the adhesion, shape, and electronic structure of Au particles supported on TiO_2(1 1 0) to further understand the catalytic activity of small supported Au particles. It was generally agreed that Au particles bind more strongly to a defective surface than to a defect-deficient surface, and that there is significant charge transfer from the support to the Au particles [24,67–71]. Lopez et al., have shown [67] that Au particles do not bind to a perfect TiO_2 surface, but have a binding energy of approximately 1.6 eV to a TiO_2 oxygen vacancy. The nature of the support then has a direct effect on the distribution and dynamics of the oxygen vacancies and determine the dispersion and shape of the Au particles, which in turn affect the catalytic activity. This key role of vacancy sites was confirmed experimentally by demonstrating that the critical coverage of Au islands at which transformation from 2-D to 3-D occurs is critically dependent on defect density [40,41,72,73]. DFT calculations show [74] that on the defect-free rutile $TiO_2(1\,1\,0)$ surface, 2-D or quasi-2D structures are metastable with respect to 3-D ones.

Utilizing high resolution STM combined with DFT calculations, Wahlstrom et al. [68] showed that bridging oxygen vacancies are the active nucleation sites for Au particles on rutile $TiO_2(1\,1\,0)$, and that each vacancy site can bind three Au atoms on average. The adsorption energy of a single Au atom on an oxygen vacancy site is more stable by 0.45 eV than on the stoichiometric surface. Au bonding on the stoichiometric surface originates via bond polarization whereas the Au-vacancy bond is covalent with very little (if any) charge transfer. These results are in contrast to those for Au adsorption on a vacancy on MgO where significant charge transfer has been postulated [69]. The electron transfer was found to occur from the six-fold Ti atom to the Au atom for a Ti-rich surface [70]. Selective deposition of Au_n^+ onto a $TiO_2(1\,1\,0)$ surface indicates via XPS that Au binds at surface oxygen vacancies forming zero valent Au_n, whose reactivity is strongly dependent on deposited particle size [75]. By combining synchrotron-based high-resolution photoemission and DFT calculations, Rodriguez et al. [24], found that nanoparticles of Au on TiO_2 are much more chemically active than metallic Au or stoichiometric titania with respect to the adsorption dissociation of SO_2. The interaction between Au particles and TiO_2 electronically perturb Au to make it more chemically active. The reactivity of titania, in turn, is also enhanced by the Au facilitating the migration of oxygen vacancies from the bulk to the surface of the oxide.

Electron transfer to Au nanoparticles has been probed by exciting TiO_2 nanoparticles coated with Au nanoparticles with CW and pulsed laser excitation [76]. By referencing to a C-60/C-60(-) redox couple, the Fermi level of the TiO_2–Au composite system was measured to be Au particle size-dependent with a shift of 20 mV for 8 nm, 40 mV for 5 nm and 60 mV for 3 nm Au nanoparticles. Using photoelectron spectroscopy (PES) and STM [77], a shift of the O 2p nonbonding state toward the Fermi level coupled with a decrease in the intensity and ultimate disappearance of the Ti 3d states were observed in the valence band with increasing Au coverages. These changes in the valence band structure presumably result from electron transfer from the surface defects on $TiO_2(1\,1\,0)$ to the Au particles, yielding electron-rich Au particles. The magnitude of the electron transfer was largest for Au particles of 3 nm or less, the size range that shows the highest catalytic activity.

On MgO, temperature-programmed reaction (TPR) studies of the catalyzed combustion of CO on size-selected, mono-dispersed Au_n ($n \leq 20$) Au particles combined with DFT simulations indicate partial electron transfer from the surface to the Au particle. Furthermore oxygen-vacancies (F-center) are purported to play a key role in the activation of nano-scale Au particles as catalysts for CO oxidation [69]. Recently in our group [78], a direct correlation has been found between the activity of Au particles for the catalytic oxidation of CO and the concentration of F-centers at the surface of a MgO support, implying a critical role of surface F-centers in the activation of Au in Au/MgO catalysts (Fig. 6). The Au particle size was measured with transmission electron microscopy and found to average 4.3 nm on the 1073 K annealed MgO support and 3.8 nm on the 1173 K annealed sample, consistent with an enhanced stability of Au particles bound to a defect-rich MgO surface [69,79].

Hammer et al. [80,81] report that in addition to serving as a structural promoter to anchor the Au particles, MgO also assumes an active role in the bonding and activation of adsorbates bound to the Au. The most reactive site for Au/MgO is formed at the Au–MgO interface whereby several low-coordinated Au atoms along with Mg^{2+} cations can interact simultaneously with an adsorbate. A direct effect of the support was also shown for the $Au/IrO_2/TiO_2$ system [82], where CO and O_2 adsorb on the IrO_2 surface and Au promotes O_2 dissociation to supply atomic O.

For Au/TiO_2, several experimental [33,83–86] and theoretical [87,88] studies show that TiO_2 provides nucleation sites for Au particles and also serves as an electron promoter, while the Au particles provide bonding sites for CO and its oxidation. The adsorption of O_2 and CO on a Au/TiO_2 catalyst do not support a Mars-van Krevelen mechanism involving lattice oxygen, implying instead reaction between molecular oxygen and CO [83]. There is evidence for adsorbed molecular O_2 on free Au_2^- and Au_4^- particles at RT, consistent with CO oxidation on the small Au particles proceeding via a di-oxygen species rather than atomic oxygen [84]. An $^{18}O_2$ isotope study [86] of Au/TiO_2 with particle size of 2–5 nm shows clear evidence of a reaction channel that does not require the dissociation of oxygen, e.g., molecularly chemisorbed oxygen can react directly with CO to form CO_2. DFT calculations [87–89] addressing the interaction of O_2 with charged and neutral Au particles, Au_n^- and Au_n ($n \leq 8$), show a pronounced sensitivity to the particle size and to the state of the charge. The interaction energy is largest for bonding with anionic Au where there is significant charge transfer to the oxygen molecule and a concomitant activation of the O–O bond to a superoxo-like state. This is consistent with excess electron in the anionic state playing a critical in O–O bond activation. Molina et al. [90], also have shown that O_2, adsorbed either at trough Ti sites or bridged-bonded between Ti and Au atom sites, are stable binding configurations. A sizable electronic charge transfer from the Au to the O_2 is reported with a concomitant electronic polarization of the support, i.e. surface mediated charge transfer. The O_2, which adsorbs on the Au particle, then reacts with CO that is adsorbed at the edge sites of the Au particles to form CO_2 with a very low (approximately 0.15 eV) energy barrier. Liu et al. [91] demonstrated that the interface between Au and the oxide can oxidize CO with a very low barrier, with the TiO_2 support enhancing the electron transfer from the Au to the antibonding states of O_2. The importance of bonding and activation of molecular O_2 on supported nano-scale Au particles deduced from theoretical calculations is consistent with the experimental observation [92] of the Freund group that CO adsorption on Au particles deposited on well-ordered alumina and iron oxide films exhibit a size effect in that small

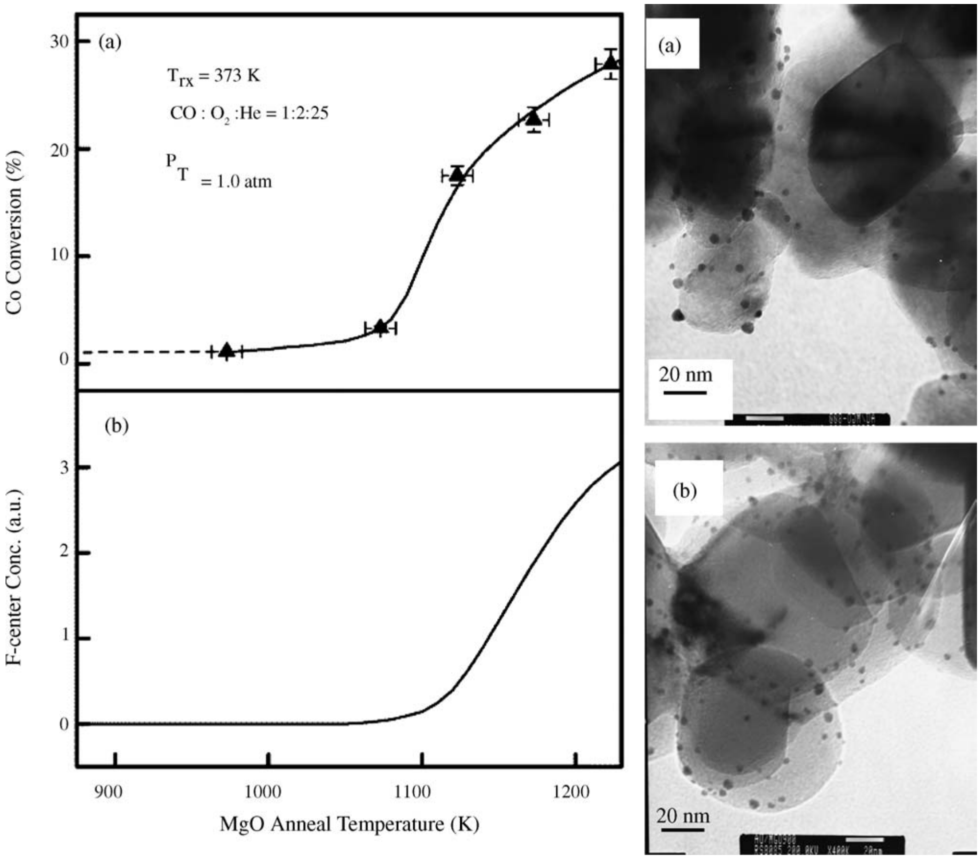

Fig. 6. (a) Conversion of CO to CO_2 by Au/MgO as a function of the anneal temperature of the MgO support prior to deposition of the Au. The data were measured at 373 K in a mixture of CO/O_2/He (1:2:25), maintaining a flow rate of 45 mL/min. (b) The relative concentration of F-centers in MgO as determined by electron energy loss spectroscopy as a function of the anneal temperature.14 Fig. 1b was adapted from Ref. [14]. (c) Transmission electron micrograph of a Au/MgO catalyst where the MgO support was annealed to 1073 K prior to deposition of the Au. (d) Transmission electron micrograph of a Au/MgO catalyst where the MgO support was annealed to 1173 K prior to deposition of the Au. [78].

particles adsorb CO more strongly, but essentially independent of the support, i.e. support effects for CO oxidation must originate from variations in the oxygen interaction with the support rather than the CO interaction.

4. Oxidation states

Gate et al. [93] have used extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge spectroscopy (XANES) to characterize the average particle size and the oxidation states of Au supported on MgO under reaction conditions. This group reports that Au^+ and Au^0 are present in the working catalysts, and that the relative amounts of each depend on the composition of the reactants. Evidence for the presence of cationic Au and zero-valent Au in the working catalyst for CO oxidation was reported [94] using a combination of temperature-programmed reduction (TPR) and temperature-programmed oxidation (TPO), and a relationship found between the activity and the amounts of cationic and zero-valent Au (Fig. 7). These results suggest that higher concentrations of cationic Au result in higher catalytic activity [93]. Since the average size of the Au particles in each of these catalysts was essentially the same as evidenced by EXAFS, the changes in catalytic activity were thus proposed to correlate with the changes in the oxidation state of Au. Similar results [95] have been reported for co-precipitated Au/Fe_2O_3, where two CO adsorbed species corresponding to CO bonded to Au^+ and Au^0, coexist upon exposure to a CO/O_2 mixture. From the relationship between the reactivity for CO oxidation and the IR intensities of CO adsorbed on Au^+ and Au^0, these authors

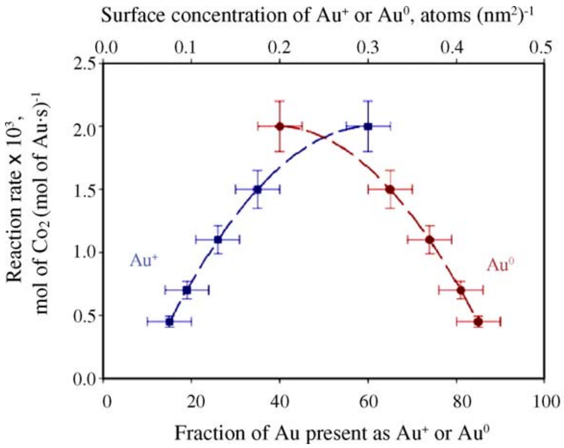

Fig. 7. Correlation of the catalytic activity with the percentage and surface concentration of cationic and zero-valent Au (the concentrations of Au were calculated on the basis of the approximate surface area of MgO). [93].

conclude that Au^+ is the more active species for CO oxidation, but is less stable than Au^0. For nano-sized Au- or Pt-ceria catalysts [17], on the other hand, it was found that metallic particles do not participate in the reaction for the water–gas shift reaction, but nonmetallic Au or Pt species, associated with surface cerium–oxygen groups, are responsible for the activity.

Gates and coworkers recently reported [96] that on zeolite NaY, a Au^{3+} complex exhibits an order of magnitude higher catalytic activity than does the Au^+ complex. XANES and infrared of adsorbed CO indicate that the loss of catalytic activity for CO oxidation during realistic reaction conditions correlate with the reduction of Au^{3+} to Au^+. It is noteworthy that the activities of Au^+ and Au^{3+} for CO oxidation are much lower than the most active high surface area supported Au catalysts [93,96], indicating that structural changes may have occurred during the reduction. The lower activity for CO oxidation catalysis on the supported Au cations compared to a catalyst containing mixtures of cationic and zero-valent Au was explained as possibly due to the fact that zero-valent Au serves as a reservoir for adsorbed CO which then spills over to Au cations at the Au-support interface where the reaction is proposed to take place [35,96].

In contrast to the above studies, recent studies of the effect of structure and activity of Au particles supported on nanocrystalline and mesoporous TiO_2 indicate that the most active state for Au supported on various allotropic structures of TiO_2 corresponds to Au in a fully reduced state [97]. Furthermore, once reduced, no reoxidation occurs under reaction conditions, even with flowing air at elevated temperatures (150 and 300 °C). These results show that oxidized Au is not necessary for high activity. On a solution prepared Au/TiO_2 [98] and Au/gamma-Al_2O_3 [99] catalysts, Au was also found to transform from Au^{3+} in as-prepared catalysts to metallic Au under air at 200 °C. Furthermore, the catalytic activity for CO oxidation (at 5 °C) increased with the percentage of metallic Au indicating that zero-valent Au is necessary for catalytic activity. On a Au/FeO_x/SiO_2/Si(1 0 0) model catalyst prepared by pulsed laser deposition (PLD) [100], with Au particle sizes of 3.8, 4.1, and 5 nm, activity for CO oxidation was related to the presence of metallic Au. These authors further purposed that the support should be amorphous and that the reaction takes place at the perimeter of Au particles.

5. From nanoparticle to well-ordered Au films

Though Au nanoparticles have been the most widely studied catalyst system in the last decade, the structure of the active site has remained elusive, due to its intrinsic complexity. The active sites are on or at the perimeter of ultra-small Au particles that are inherently difficult to structurally characterize, and are supported on a catalyst surface that is extremely heterogeneous and poorly defined. As discussed above, the special catalytic properties of nanostructured Au particles have been associated with a special particle size of ~3 nm that consists of a bi-layer island, support effects, particle shape or perimeter, the Au-oxide support contact area, and the metal oxidation state. Recently, our group [33,101] reported an atomic-level, structure-activity relationship for the catalytic activity of supported Au that represents an important step toward identification of the active site. Specifically, two well-ordered Au films, a (1 × 1) monolayer (ML) and a (1 × 3) bilayer, that completely wet an ultrathin titanium oxide (titania) surface, were grown on a Mo(1 1 2) surface. Unprecedented catalytic activity for CO oxidation was observed for the Au bilayer structure (Fig. 8).

The Mo(1 1 2)-(8 × 2)-TiO_x support was grown on the Mo(1 1 2) by depositing 1 ML of Ti onto a Mo(1 1 2)-$c(2 \times 2)$-[SiO_4] surface [102] following subsequent oxidation and annealing [33]. The TiO_x film so formed exhibited a sharp (8 × 2) low energy electron diffraction (LEED) pattern and a planar surface as reflected by the STM images shown in Fig. 9. From the observed single phonon feature 84 meV (Fig. 10), the oxidation state was proposed to be 3+ [33,103], consistent with parallel XPS studies.

Au was found to completely wet the Mo(1 1 2)-(8 × 2)-TiO_x surface forming two well-ordered structures, Mo(1 1 2)-(1 × 1) and -(1 × 3) at Au coverages of 1.0 and 1.33 ML, respectively, as reflected in a sharp LEED pattern (Fig. 11) and the linear relation of the Au/Mo AES ratio versus deposition time (Fig. 12). Wetting of the TiO_x surface by Au is also consistent with recent STM and TPD studies. The formation of Au films was confirmed by the appearance of a pronounced CO vibrational feature [(CO)] at 261 meV (2088 cm^{-1}) upon CO adsorption at 90 K (Fig. 10B, inset), whose vibrational frequency is very near to those observed on metallic Au

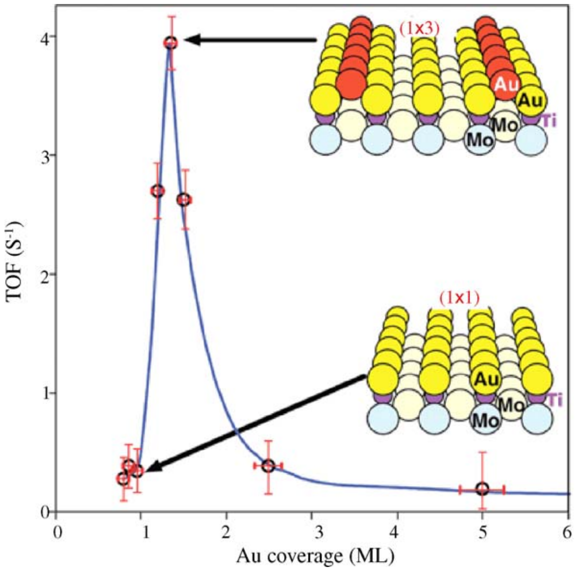

Fig. 8. Activity for CO oxidation at room temperature as a function of Au coverage above the monolayer on Mo(1 1 2)-(8 × 2)-TiO_x. The CO:O_2 ratio was 2:1, and the total pressure was 5 Torr. The data represent initial rates derived by extrapolating the rate data to zero time. The TOF frequency for the (1 × 1) Au structure was calculated with the total number of Au atoms in the structure; we computed the TOF for the (1 × 3) structure by dividing the overall rate minus two-thirds the (1 × 1) rate (those reactive atom sites blocked by the second-layer Au) by the number of Au atoms in the second layer of the structure; for Au coverages >2.0 ML, the TOFs are based on total Au due to the formation of 3-D particles. Insets: schematic models for the (1 × 1) and (1 × 3)-Au/TiO_x surfaces.

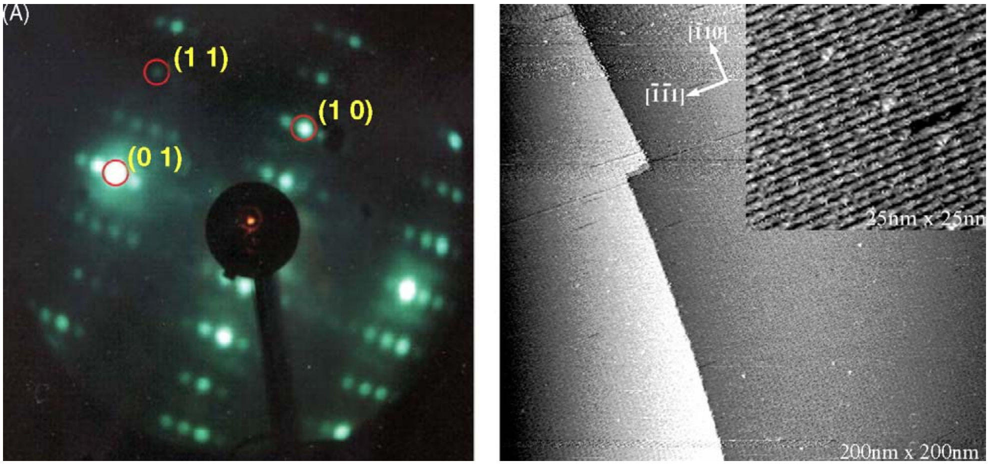

Fig. 9. LEED patterns and STM image of the Mo(1 1 2)-(8 × 2)-TiO_x [33,110].

surfaces. Au atoms were proposed to bind directly to a coordinatively unsaturated Ti atoms at a-top or bridging sites (Fig. 11), as reported for Au on TiO_2(1 1 0) [34,68,104]. The direct bonding between Ti and Au is evident in the significant blue-shift and broadening of the Ti–O phonon feature (Fig. 10, curve d). This feature can be qualitatively deconvoluted into two components, one at 90 meV and another at 100 meV, which correspond to asymmetrical stretching of Ti^{4+}–O–Mo and Ti^{4+}–O–Ti^{4+} species, respectively [33]. These data imply that the TiO_x layer, in bonding to Au and rearranging from the (8 × 2) to the (1 × 1) structure, is oxidized, consistent with the formation of $Au^{\delta-}$ [34,68,104], which was confirmed by recent XPS data. The arrangement of the Au atoms is similar to that in the Au(1 1 0) surface, but with the nearest Au–Au distance of 2.73 Å, corresponding to the Mo(1 1 2) lattice. CO remains adsorbed on this Au surface up to 150 K, corresponding to a significant stabilization compared to 100 and 125 K for Au(1 1 1) and Au(1 1 0), respectively [105,106].

In the (1 × 3) structure, a second row of Au atoms is located above the first layer of Au atoms as displayed in Fig. 12. Upon formation of this bilayer structure, the (CO) blue-shifts slightly to a frequency very near that of metallic Au. The intensity of the CO band relative to the Ti–O phonon feature for saturation CO coverage at 90 K increases with increasing Au coverages up to 1 ML; the intensity then decreases.

The catalytic efficacy of the discrete (1 × 1) and (1 × 3) structures of Au on TiO_x–Mo(1 1 2) was tested for CO oxidation at realistic reaction conditions [35] as a function of the Au coverage (Fig. 8) [33]. The initial turnover frequencies (TOFs) for CO oxidation at room temperature over the (1 × 1)

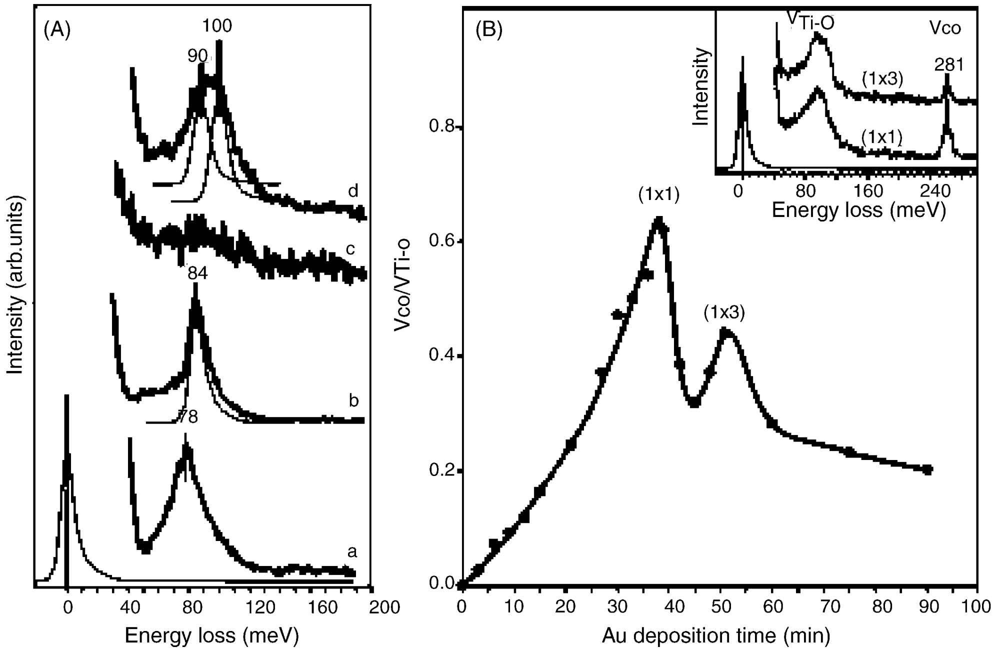

Fig. 10. (A) HREEL spectra for (a) Mo(1 1 2)-O annealed at 1400 K; (b) the Mo(1 1 2)-(8 × 2)-TiO_x; (c) 1 ML Au deposited on the Mo(1 1 2)-(8 × 2)-TiO_x at room temperature; and (d) the material in (c) after annealing at 900 K for 10 min. (B) Relative intensities of (CO)/(Ti-O) vs. Au deposition onto the Mo(1 1 2)-TiO_x surface; CO was adsorbed to saturation at 90 K. Inset: HREEL spectra after CO adsorption on the (1 × 1) and (1 × 3) surfaces. [33].

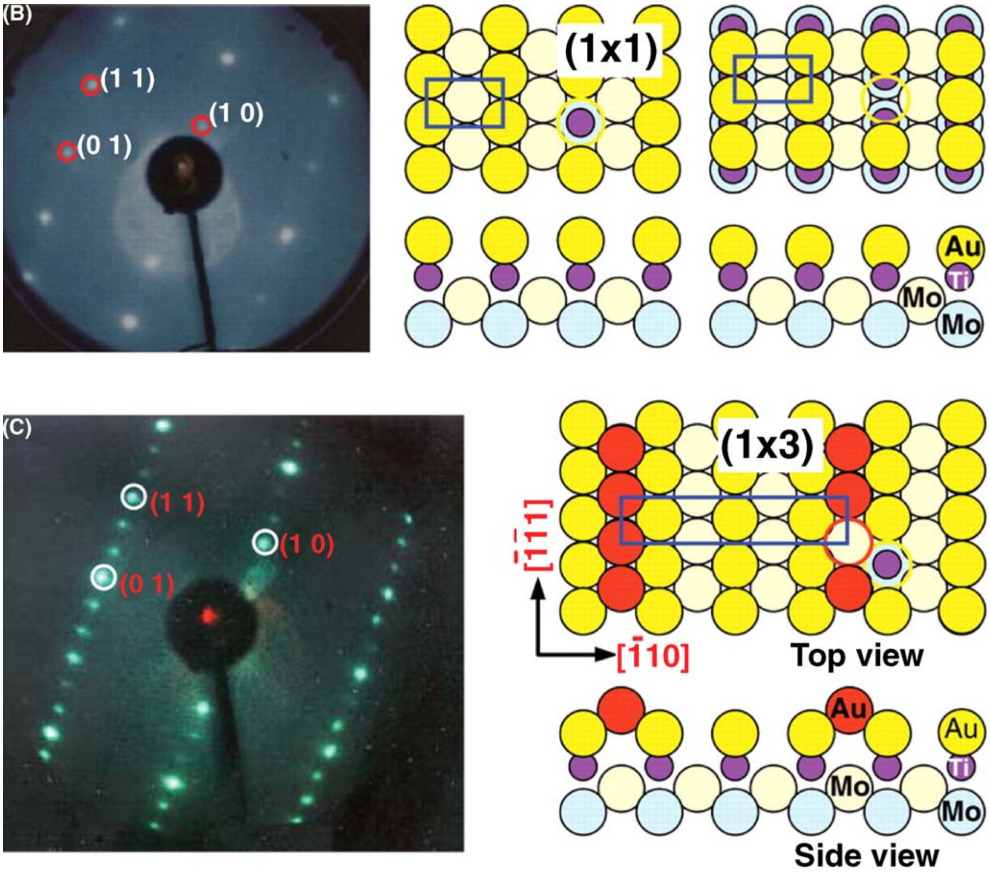

Fig. 11. LEED patterns and structural models, top and side views for (A) the Mo(1 1 2)-(1 × 1)-(TiO_x, Au); and (B) the Mo(1 1 2)-(1 × 3)-(TiO_x, Au1.33). The oxygen atoms are omitted from the models for clarity. [33].

Au (monolayer) structure were significantly lower than the rate over the (1 × 3) Au (bilayer) structure. The specific rate per unit area found for the Au-(1 × 3) surface was >45 times that previously reported for the most active high surface area Au/TiO_2 catalysts [107]. Assuming that the Au-(1 × 3) structure is the optimum catalytic morphology, a factor of 45 then represents the potential for improvement in existing supported Au catalysts for CO oxidation. At Au coverages in excess of 1.33 ML, the reaction rate falls sharply from its maximum for the Au-(1 × 3) structure, which is likely a consequence of either (i) the additional Au forming 3-D particles with low activities on the (1 × 3) structure that partially block access to the active Au-(1 × 3) surface sites and/or (ii) a decrease in the optimum ratio of the first- and second-layer Au sites. The specific rates measured in this study for the Au-(1 × 3) sites agree closely with the rates reported previously for Au particles supported on TiO_2(1 1 0), where an activity maximum was observed for Au structures with two atomic layers in thickness [27].

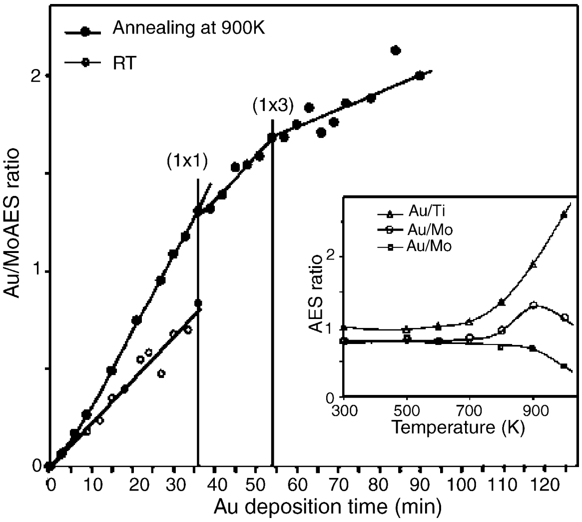

Fig. 12. Plots of Au/Mo AES ratios vs. deposition time. Inset: A plot of the indicated AES ratios as a function of the anneal temperature for 1 ML Au on Mo(1 1 2)-(8 × 2)-TiO_x. RT, room temperature. [33].

The exceptional activity of Au nanostructures for CO oxidation was often proposed to include a direct role played by the support, such as at the perimeter of the Au-support interface [3,41,80–82]. The much higher activity observed on the (1 × 3)-Au bilayer than that on the (1 × 1)-Au monolayer (Fig. 8) [33] shows that the TiO_x support is crucial as a dispersant and a promoter of the Au overlayer, but that TiO_x itself cannot be directly involved in the bonding of O_2 or CO, because in the Au-(1 × 1) and -(1 × 3) structures (Fig. 11), the Au overlayer precludes access to the Ti cation sites by the reactants. As shown in Fig. 11, the coordination numbers for Au atoms in the monolayer structure and that of the top layer in the (1 × 3) bilayer structure are essentially identical noting that one-dimension (1-D) chains of present in the monolayer, i.e. Au atoms are unable to bind with neighboring Au rows along the [−1 1 0] direction. The lower activity of the (1 × 1) monolayer surface clearly demonstrates that the interface of Au-support is not sufficient for an special CO oxidation activity, but that a combination of the first- and second-layer Au sites as shown in the (1 × 3) structure (Fig. 11) is necessary to promote reaction between CO and O_2. The interaction of the first-layer Au with Ti^{3+} of the support, yielding $Au^{\delta-}$, likely is crucial for activation of O_2 [34,68,104]. CO, however, has been shown to adsorb strongly on the Au bilayer structure [48]. For the more general case of Au/TiO_2, mono- and bi-layer Au islands in the <4 nm diameter range form as a result of Au atoms nucleating initially at Ti^{3+} defect sites [27], then with the addition of more Au, evolve into Au bilayer islands stabilized by the bonding between the interfacial Au atoms and Ti^{3+} defects that accumulate at the Au–TiO_2 interface [24]. The mono- and bi-layer Au islands seen for Au on TiO_2(1 1 0) [27] have also been observed for Au supported on high surface area TiO_2 by Lupini et al. [108]. These mono- and bi-layer Au structures appear to be truncated analogs of the extended Au-(1 × 1) and Au-(1 × 3) structures (Fig. 11) [33]. In the arrangement of the (1 × 3) surface, all the top layer Au atoms of the bilayer structure are accessible to the reactants, a morphology that may very well contribute to its exceptional catalytic activity.

Recent density functional theoretical calculations have shown that O_2 adsorbs preferentially and readily dissociates at the Au–TiO_2 interface [82]. However, as discussed above, for the Au-(1 × 3) structure, access by O_2 to the Au and Ti interface is precluded. Recent several experimental and theoretical studies [83-88,109,110] have shown that CO oxidation can take place entirely on the Au particles without any support mediation. In any case, if O_2 activation is promoted by the Au-(1 × 1) sites and CO adsorbs on the Au-(1 × 3) sites, theory predicts a relatively small barrier for the CO–O_2 reaction [90].

6. Conclusions

Based on surface science model catalyst studies, it is well established that the bilayer Au structure with appropriate morphology is a key for exceptional higher activity for CO oxidation. Defect sites on the oxide support play an important role in the wetting of Au particles yielding electron-rich Au, crucial for activating molecular O_2. But the support itself need not be directly involved in the CO oxidation reaction sequence. The presence or absence of cationic Au does not appear to be an important factor for CO oxidation. The successful synthesis of well-ordered monolayer and bilayer Au films on the TiO_x/Mo(1 1 2) and the atomic-level observation of activity–structure relationship has contributed to the detailed characterization of the active site. Due to its extraordinary activity and homogeneity of planar model catalysts, further studies both experimentally and theoretically will lead to a more thorough understanding of the unique catalytic properties of supported Au nanoparticles.

Acknowledgements

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