Catalysis Letters 56 (1998) 7–10

Structure sensitivity of CO oxidation over model Au/TiO_2 catalysts

M. Valden [b], S. Pak [a], X. Lai [a] and D.W. Goodman [a,*]

[a] *Department of Chemistry, Texas A&M University, PO Box 300012, College Station, TX 77842-3012, USA*
E-mail: goodman@mail.chem.tamu.edu
[b] *Department of Physics, Tampere University of Technology, Tampere, FIN 33101, Finland*

Received 30 June 1998; accepted 29 September 1998

Model catalysts of Au clusters supported on TiO_2 thin films were prepared under ultra-high vacuum (UHV) conditions with average metal cluster sizes that varied from $\sim$2.5 to $\sim$6.0 nm. The reactivities of these Au/TiO_2 catalysts were measured for CO oxidation at a total pressure of 40 Torr in a reactor contiguous to the surface analysis chamber. Catalyst structure and composition were monitored with Auger electron spectroscopy (AES) and scanning tunneling microscopy and spectroscopy (STM/STS). The apparent activation energy for the reaction between 350 and 450 K varied from 1.7 to 5 kcal/mol as the Au coverage was increased from 0.25 to 5 monolayers, corresponding to average cluster diameters of 2.5–6.0 nm. The specific rates of reaction ((product molecules) $\times$ (surface site)$^{-1}$ $\times$ s^{-1}) were dependent on the Au cluster size with a maximum occurring at 3.2 nm suggesting that CO oxidation over Au/TiO_2(001)/Mo(100) is structure sensitive.

Keywords: gold catalysis, CO oxidation, gold/titania, structure/activity relationships

1. Introduction

Highly dispersed Au has been shown to be active for a number of reactions including low-temperature catalytic combustion, partial oxidation of hydrocarbons, hydrogenation of carbon oxides and unsaturated hydrocarbons, and reduction of nitrogen oxides [1,2]. In particular, recent research has demonstrated that highly dispersed Au supported on reducible metal oxides such as Fe_2O_3, Co_3O_4, NiO, $Be(OH)_2$ and TiO_2 is exceptionally active for low-temperature oxidation of CO [2–5]. Since the CO oxidation over supported Au catalysts has been observed to be strongly structure sensitive, the deposition method of Au, the Au cluster–support interface, the structure/chemical composition of the support, as well as pretreatment of the catalyst are all critical parameters in determining the Au cluster morphology and, thereby, the activity of the Au catalyst. For instance, Au clusters supported on TiO_2 with varying geometries can be prepared using deposition–precipitation or impregnation methods [4]; the more dispersed Au clusters show much higher activity for CO oxidation. The higher activity of the more dispersed Au clusters has been attributed to the larger perimeter interface, which has been proposed to provide active sites for the CO and O_2 adsorption and the CO–O_2 reaction [2].

Various pretreatments of the Au/TiO_2 catalyst have also been observed to significantly influence catalytic activity for CO oxidation. A high-temperature reduction (HTR) at 773 K followed by calcination (C) at 673 K and a low-temperature reduction (LTR) at 473 K produced a Au/TiO_2 catalyst which was over two orders of magnitude more active at 313 K than for a Pd/TiO_2 catalyst [6,7]. Furthermore, the HTR/C/LTR-treated Au/TiO_2 catalyst was stable above 400 K, whereas the HTR-treated Au/TiO_2 catalyst deactivated very rapidly.

In this study, we present reaction kinetics data of CO oxidation over Au clusters supported on TiO_2 thin films. The catalytic activity is found to be strongly dependent on the Au cluster size. The specific rate of CO oxidation is observed to exhibit a maximum at a cluster size of 3.2 nm with an electronic structure characterized by a band gap of $\sim$0.4 V based on our STM/STS measurements, suggesting a correlation between the local electronic properties and the catalytic activity of supported gold nanoclusters.

2. Experimental

Experiments were performed in two ultra-high vacuum (UHV) chambers. One of these chambers had a base pressure of 6×10^{-10} Torr and was equipped with a single-pass cylindrical-mirror analyzer for Auger electron spectroscopy (AES), a quadrupole mass analyzer for temperature-programmed desorption (TPD) and a contiguous high-pressure reactor for reaction kinetics studies. The reaction products were extracted from the reactor with a vacuum syringe, where the gas mixture was compressed and then injected into a gas chromatograph (GC) for analysis. A Varian 3400CX series GC with a thermal conductivity detector (TCD) and Hyesept D, 40-foot column was employed in this study. The reaction kinetics were carried out at a total pressure of 40 Torr using a CO : O_2 (1 : 5) gas mixture.

The model Au/TiO_2 catalysts were prepared by vapor deposition of Au onto a thin film of TiO_2 supported on Mo(100). The TiO_2 thin films were synthesized by expos-

---

[*] To whom correspondence should be addressed.

ing the clean Mo(100) surface to an evaporated flux of Ti in an O_2 ambient of 5×10^{-7} Torr and subsequently annealing to 1100 K. This procedure has been shown to produce a fully stoichiometric and epitaxial thin film of TiO_2(001) [8].

The Au clusters were deposited by thermal evaporation from a source containing high-purity Au wire wrapped tightly around a W filament, which was heated resistively. The Au clusters grow in the form of three-dimensional islands at 350 K according to the Volmer–Weber growth mode [8]. After deposition, the model Au/TiO_2(001)/Mo(100) catalysts were annealed to 600 K which has been shown to thermally stabilize the Au clusters [8]. The surface composition of the model catalysts was monitored by AES before and after the high-pressure reactions; temperature was measured with a W–5%Re/W–26%Re thermocouple spot-welded to the sample.

The STM experiments were performed in a second UHV chamber using a UHV-STM (Omicron). Constant current topographic (CCT) images were obtained by biasing the sample at +2.0 V. The STS spectra were recorded during the CCT imaging by stopping the scan at a certain point of interest, interrupting the STM feedback loop and measuring the tunneling current as a function of the bias voltage. These I–V curves can then be correlated with the corresponding geometric features of the surface.

3. Results and discussion

The growth of ultrathin oxide films on refractory metals provides a convenient way to overcome many of the experimental difficulties related to the bulk oxides. Recent results in our laboratories have demonstrated that thin films with thickness greater than a few monolayers (ML) are adequate to simulate the physical and chemical properties of the bulk-terminated surfaces of metal oxides such as SiO_2, MgO, NiO, Al_2O_3, and TiO_2 [9].

Figure 1 shows the average diameter of Au clusters as a function of the Au coverage in ML for Au/TiO_2(110) and Au/TiO_2(001)/Mo(100). The Au coverages were determined by Au desorption that was calibrated using the corresponding desorption spectrum obtained from 1 ML of Au [8]. The Au films were deposited at room temperature and annealed to 600 K; the average particle shape and diameter were measured using STM.

Since the (001) face of TiO_2 is thermodynamically unstable at temperatures above 650 K, the surface structure of the TiO_2(001)/Mo(100) film is atomically rough [10]. This inherent roughness of the TiO_2(001) surface makes high-resolution STM imaging of the Au clusters supported on TiO_2(001)/Mo(100) extremely demanding. Therefore, in addition to the STM measurements performed for Au/TiO_2(001)/Mo(100), a set of STM measurements was also acquired from Au/TiO_2(110) as in [11]. Both data sets were then combined in order to convert the Au coverage to the average cluster diameter using a polynomial fit (solid line in figure 1).

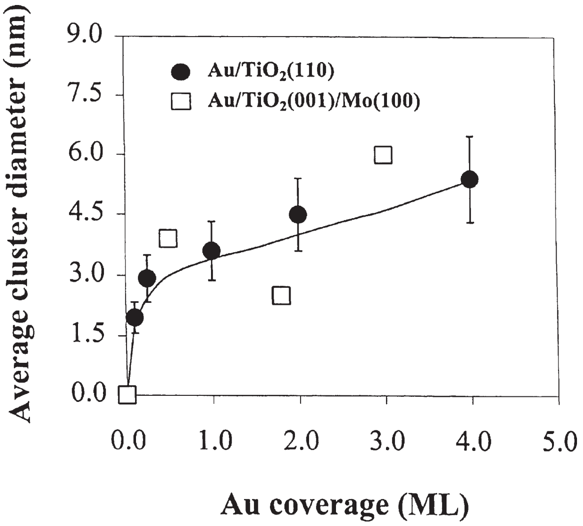

Figure 1. Average Au cluster diameter as a function of Au coverage in monolayers (1 ML = 1.387×10^{15} atoms/cm^{-2}) for gold clusters supported on TiO_2(110)-(1×1) and thin film of TiO_2(001)/Mo(100). The gold was deposited at 300 K followed by an anneal to 600 K. The solid line represents a polynomial fit for the Au/TiO_2(110) and Au/TiO_2(001)/Mo(100) data.

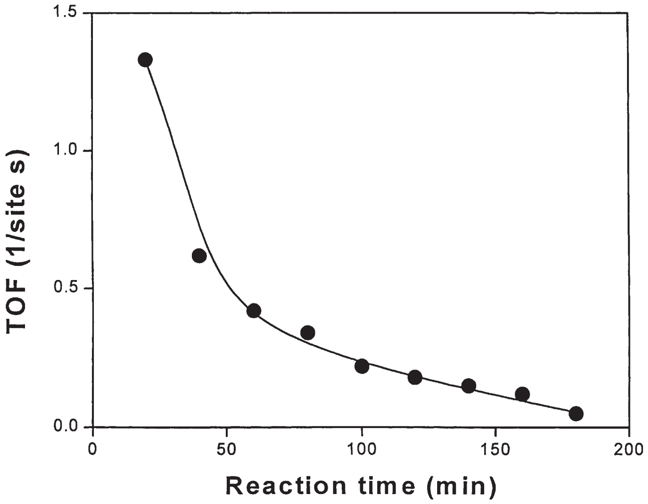

Figure 2. The specific activity for CO conversion as a function of reaction time at 300 K on a model Au/TiO_2(001)/Mo(100) catalyst. The gold coverage was 0.25 ML corresponding to an average cluster size of ~2.4 nm.

The catalytic properties of the TiO_2-supported Au catalysts were investigated for the CO–O_2 reaction from 300 to 450 K. Figure 2 shows activity for CO oxidation at 40 Torr of CO/O_2 (1 : 5) as a function of reaction time at 300 K for 0.25 ML Au/TiO_2(001)/Mo(100) with an average Au cluster size of ~2.4 nm. The activity is expressed as the specific reaction rate ((product molecules) × (surface site)$^{-1}\times s^{-1}$) or turnover frequency (TOF). The Au catalyst exhibits a high initial activity, however, the catalyst deactivates rapidly. The surface composition was monitored by AES showing a carbon peak after the first 20 min of the reaction whose intensity increased with reaction time. After reaction for 150 min, the catalyst was exposed to 40 Torr

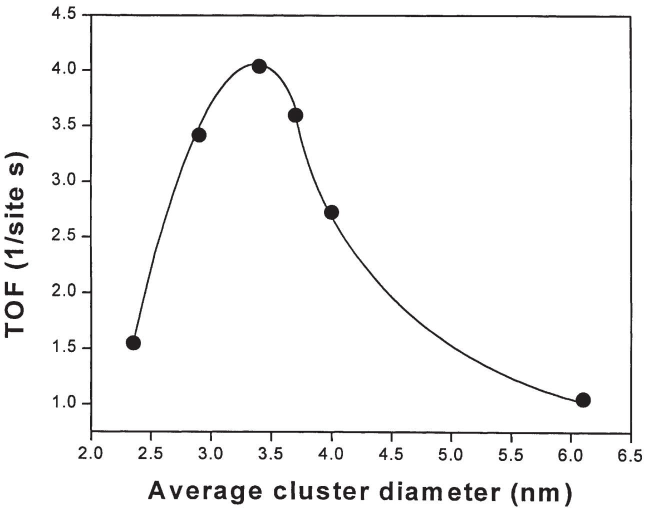

Figure 3. The specific activity for CO conversion as a function of average Au cluster diameter on Au/TiO_2(001)/Mo(100) at 350 K. The number of surface sites was computed using the cluster morphology determined by STM. $P_{\text{total}} = 40$ Torr, CO/O_2 = 1/5.

of O_2 at 600 K for 1 h. This procedure cleaned the carbon contamination, however, with no subsequent increase in the activity of the catalyst. Therefore, it is unlikely that the deactivation is solely due to the blocking of the active sites by carbon.

Although thermally stable Au catalysts are formed during the catalyst preparation [8], adsorbate-induced morphological changes of the Au clusters can occur during CO oxidation even at 300 K. 0.25 ML Au on TiO_2(110)-(1 × 1), exposed to 10 Torr of CO : O_2 or O_2 at 300 K for 120 min, showed a dramatic enhancement of the Au cluster size [11]. The initial cluster size of ~2.6 nm in diameter and ~0.7 nm in height increased to ~3.6 nm in diameter and ~1.4 nm in height after the exposure. Since the activity of Au/TiO_2 strongly depends on the Au cluster size, decreasing as the cluster size increases, the deactivation shown in figure 2 is likely due to agglomeration of the Au clusters.

Figure 3 shows the initial (20 min reaction) specific reaction rate for CO oxidation at 350 K and 40 Torr of CO/O_2 (1 : 5) as a function of gold cluster size. The TOFs for each Au cluster size were computed using the average cluster shape and size as measured with STM. The specific reaction rate increases with particle size to a maximum at ~3.2 nm followed by a decline in activity with a further increase in size. This is identical to the behavior observed for high-surface-area Au/TiO_2 catalysts [4,11].

Figure 4 shows the apparent activation energy (E_a) for CO oxidation at 350 K and 40 Torr of CO/O_2 (1 : 5) as a function of cluster diameter. The lowest E_a (3.5 kcal/mol) on ~3.0 nm clusters is similar to that of a high-surface-area Au/TiO_2 catalyst (4.5 kcal/mol) with an average size of 3.1±0.7 nm in diameter [4]. This significant variation in the apparent activation energy of the reaction as a function of cluster diameter is inconsistent with a perimeter interface model of [4], but rather suggests an intrinsic variation in the reaction activation parameter as a function of cluster size.

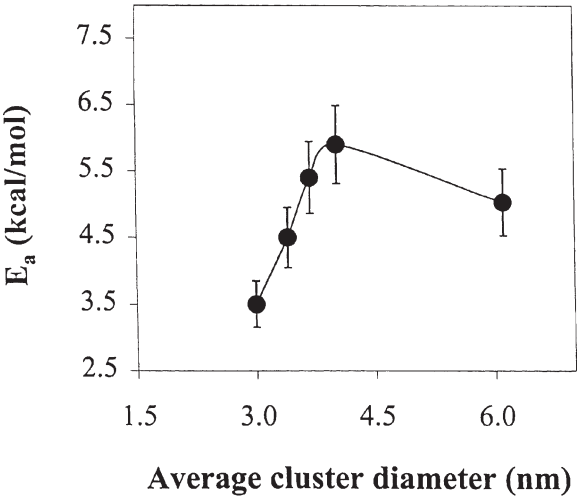

Figure 4. Apparent activation energy E_a as a function of average Au cluster diameter on Au/TiO_2(001)/Mo(100) at 350 K.

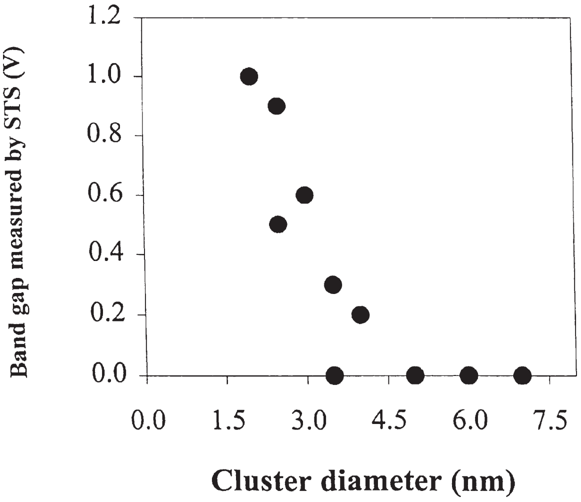

Figure 5. Gold cluster band gap measured by STS as a function of the cluster size on Au/TiO_2(001)/Mo(100). The band gaps were measured for various Au coverages ranging from 0.5 to 3.0 ML corresponding to cluster diameters ranging from 1.5 to 7.0 nm.

In order to investigate the possible correlation between the electronic properties and the specific activity of the Au clusters in more detail, STS measurements were carried out on the Au/TiO_2(001)/Mo(100) catalysts. The STS data were acquired by simultaneously recording the corresponding topographic images. This procedure allows us to investigate the electronic properties of *individual* nanometer-size Au clusters. Figure 5 summarizes these STS measurements in terms of the band gap of the Au clusters as a function of cluster diameter. A metal to non-metal transition is apparent as the cluster size approaches approximately ~4.0 nm in diameter (~400 atoms/cluster), the approximate size at which onset of catalytic activity is observed for CO oxidation. These data strongly suggest that the specific activity of Au/TiO_2(001)/Mo(100) is determined by the unique electronic structure of Au clusters which exhibit a band gap of $\sim$0.4 V as measured by STS. Furthermore, a more detailed analysis of the cluster morphology reveals those clusters with optimum activity have a thickness of two atomic layers of Au [11].

Recently, Okumura et al. have examined the influence of the metal oxide support on the catalytic activity of gold for CO oxidation [12]. The specific activities of Au/SiO_2, Au/Al_2O_3 and Au/TiO_2 were found to be essentially independent of the support material provided that the Au cluster sizes were sufficiently small. Apparently, then the catalytic activity of Au/TiO_2 for the low-temperature CO oxidation is defined primarily by the intrinsic electronic structure of the Au clusters.

4. Conclusions

Reaction kinetics has been studied for low-temperature CO oxidation over Au clusters supported on TiO_2 thin films. The specific rate and apparent activation energies are observed to depend strongly on the Au cluster size. The specific activity increases with the Au cluster diameter to a maximum value for $\sim$3.2 nm clusters whose electronic properties are characterized by a band gap of $\sim$0.4 V as measured by STS and then declines. It is proposed that the pronounced structure sensitivity of CO oxidation on metal-oxide-supported Au nanoclusters is mainly determined by the changes of the electronic properties of the Au clusters as a function of their size, with Au clusters of two atomic layers thick being optimum.

Acknowledgement

We acknowledge with pleasure the support of this work by the Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, the Robert A. Welch Foundation, the Dow Chemical Company and the Academy of Finland.

References

[1] M. Haruta, Catal. Surveys Jpn. 1 (1997) 61.
[2] M. Haruta, Catal. Today 36 (1997) 153 and references therein.
[3] M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M.J. Genet and B. Delmon, J. Catal. 144 (1993) 175.
[4] G.R. Bamwenda, S. Tsubota, T. Nakamura and M. Haruta, Catal. Lett. 44 (1997) 83.
[5] Z.M. Lin and M.A. Vannice, Catal. Lett. 43 (1997) 51.
[6] M.A. Bollinger and M.A. Vannice, Appl. Catal. B 8 (1996) 417.
[7] S.D. Lin, M. Bollinger and M.A. Vannice, Catal. Lett. 17 (1993) 245.
[8] C. Xu, W.S. Oh, G. Liu, D.Y. Kim and D.W. Goodman, J. Vac. Sci. Technol. A 15 (1997) 1261.
[9] S.C. Street, C. Xu and D.W. Goodman, Ann. Rev. Phys. Chem. 48 (1997) 37 and references therein.
[10] G.E. Poirier, B.K. Hance and J.M. White, J. Phys. Chem. 97 (1993) 5965.
[11] M. Valden, X. Lai and D.W. Goodman, Science (11 September 1998) 1647.
[12] M. Okumura, S. Nakamura, S. Tsubota, T. Nakamura, M. Azuma and M. Haruta, Catal. Lett. 51 (1998) 53.