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Enhanced activity for supported Au clusters: Methanol oxidation on Au/TiO_2(110)

Samuel A. Tenney, Brett A. Cagg, Mara S. Levine, Wei He, Kedar Manandhar, Donna A. Chen *

Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208, United States

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ABSTRACT

Gold clusters supported on TiO_2(110) exhibit unusual activity for the oxidation of methanol to formaldehyde. Temperature programmed desorption studies of methanol on Au clusters show that both Au and titania sites are necessary for methanol reaction. Isotopic labeling experiments with CD_3OH demonstrate that reaction occurs via O–H bond scission to form a methoxy intermediate. When the TiO_2 surface is oxidized with $^{18}O_2$ before or after Au deposition, methanol reaction produces $H_2^{18}O$ below 300 K, indicating that oxygen from titania promotes O–H bond scission and is incorporated into desorbing products. XPS experiments provide additional evidence that during methanol reaction on the Au/TiO_2 surface, methanol adsorption occurs on TiO_2, given that the titania support becomes slightly oxidized after exposure to methanol in the presence of Au clusters. While the role of TiO_2 is to dissociate the O–H bond and form the reactive methoxy intermediate, the role of the Au sites is to remove hydrogen from the surface as H_2, thus preventing the recombination of methoxy and hydrogen to methanol. The decrease in formaldehyde yield with increasing Au coverage above 0.25 ML suggests that reaction occurs at Au–titania interfacial sites; scanning tunneling microscopy images of various Au coverages confirm that the number of interfacial sites at the perimeter of the Au clusters decreases as the Au coverage is increased between 0.25 and 5 ML.

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1. Introduction

Recently there has been great interest in the catalytic properties of Au nanoclusters for low temperature oxidation [1–10] and epoxidation [11] reactions. Despite the inertness of bulk Au surfaces, Au nanoclusters supported on titania have excellent selectivity for the low temperature epoxidation of propene with O_2, [11]. One of the major challenges in catalysis today is the development of a heterogeneous catalyst for the direct epoxidation of propene to propene oxide using molecular oxygen, given that propene oxide is a starting material for many organic synthesis products and represents a multibillion dollar industry for the production of 3.5 million tons of propene oxide/year [12,13]. Furthermore, Au nanoclusters on titania and other reducible metal oxide supports are known to be good catalysts for the low temperature oxidation of CO to CO_2 [2–6,14,15]. The ability to oxidize CO at low temperature is especially important for fuel cell applications [16–18] and for CO removal in automobile engines under cold start conditions [19] because the current automotive catalysts are not effective below 200 °C [20].

The surprising activity of titania-supported Au nanoclusters of less than 40 Å in diameter compared to the inactive bulk Au surfaces has been a topic of much discussion in the literature [8,10,21]. In particular, there have been many studies of CO oxidation on supported Au clusters, but the origins of the increased activity for the Au nanoclusters are not completely understood and are still a topic of controversy. Many factors are reported to influence the activity of the Au clusters, including electronic effects [22], interactions with the support [23–26], particle size [22,25,27–29], the nature of sites at the particle surface [31,39], the oxidation states of Au [6,32,33], the method of catalyst preparation [5] and the amount of residual chloride from the Au precursor [15].

Density functional theory (DFT) studies provide strong evidence that the unusual activity of the small Au clusters is due to the greater number of active, undercoordinated Au atoms at the surfaces of the clusters [31,39]. There is also good evidence that for reactions like CO oxidation, the enhanced activity of Au clusters on titania stems from the unique geometries of atoms on the cluster surfaces. DFT studies of supported Au clusters by the Norskov group have demonstrated that undercoordinated Au atoms on the Au clusters play an important role in the CO oxidation activity [31,34–40]. Activity of the clusters scales with the fraction of low coordination number Au atoms rather than the surface area of the clusters [31,36,37]. The binding energy of CO, atomic O and O_2 all decrease linearly with increasing coordination number of the Au atoms [36,41], and CO adsorption properties [28], as well as O_2 dissociation [38], are dominated by the activity of the undercoordinated Au atoms. Thus, activity of the small particles arises from the high fraction of atoms with special geometries, such as corner and edge atoms, rather than from their intrinsic size [36,39]. There are also experimental studies of Au on metal oxide supports that corroborate the idea that the unusual activity of the clusters can be explained by the high fraction of undercoordinated atoms with special geometries like corner and edge sites [42–44].

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* Corresponding author. Tel.: +1 803 777 1050; fax: +1 803 777 9521.
E-mail address: dachen@sc.edu (D.A. Chen).

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While the importance of undercoodinated Au atoms is generally accepted, conflicting reports exist in the literature regarding the effects of cationic Au, the potentially unique activity of two-layer Au clusters, and the role of the support. For example, it has been proposed that cationic Au at the edges of the clusters is responsible for the enhanced CO oxidation activity. Gates and co-workers showed that for MgO-supported Au catalysts prepared from a Au(III) complex, the catalyst was more active when there was a higher concentration of Au(I) compared to metallic Au [32]. In contrast, Goodman and co-workers have investigated Au clusters vapor-deposited on crystalline titania surfaces and found that the presence of cationic Au is not an important factor in the enhanced activity of the clusters [45,46]. The Goodman group also reported that bilayer Au clusters on TiO_2 had significantly higher activity for CO oxidation than monolayer clusters or more three-dimensional Au clusters [45,47]. Furthermore, a STEM study of Au on FeO_x catalysts showed that high activities were correlated with the presence of bilayer clusters of 0.5 nm in diameter [48]. However, the presence of bilayer clusters was not necessary for high activity of Au on an iron oxide support [49].

There is also compelling evidence that the Au–titania interface and associated active sites play an important role. Au clusters on highly reducible supports like ceria, titania and iron oxide exhibit higher activity than on nonreducible supports like AgO, alumina and silica [14,50], even for clusters of the same size range [51], and Au on TiO_2 is 2–3 times more active than Au on SiO_2 for CO oxidation [52–54]. Indeed, it has been proposed that both oxidation [4,55] and epoxidation [11,56,57] occur at the interface between the perimeter of the Au clusters and the titania support. Titania layers grown on inactive Au powder with 10 μm crystallites have high activity for CO oxidation, similar to the 3.5 nm Au particles on titania [53,54,58]; a study of titania clusters grown on Au(111) further demonstrates that the Au–titania interfacial sites are the active sites since this surface has the same activity for the water gas shift reaction as Au clusters grown on titania [59]. In addition, hemispherically shaped Au clusters on titania show greater activity for CO oxidation than spherically shaped clusters, and the increase in activity is attributed to the greater contact area between the support and the hemispherical clusters [2,6,60]. DFT [55] and experimental investigations [25] also report that the Au–titania interfacial sites are the active sites for CO oxidation, and in the proposed mechanism, CO is adsorbed on Au while O_2 is activated on titania. A similar mechanism was suggested for Au clusters on Fe_2O_3, which is another highly reducible support [50]. Moreover, DFT calculations indicate that the active surface species is bound to both the Au cluster and the support [38,61,62]. Recent work by the Yates group shows that the dissociation of O_2 occurs at the Au–titania interface via the formation of a $CO–O_2$ complex, and therefore reaction occurs at the perimeter of the clusters [63].

In other cases, the support is believed to play only a minor, secondary role [14]. For Au clusters on TiO_2, $MgAl_2O_4$ and Al_2O_3 supports, the differences in activity could be explained by the number of low coordination sites in the clusters, based on particle sizes measured in STEM and EXAFS as well as a geometric calculation; it was therefore not necessary to invoke particle–support interactions to explain enhanced activities [44]. DFT investigations report that the interfacial energy between the Au cluster and support determines the cluster dispersion, shape and structure, which in turn influences the number of active, low coordination Au sites [37]. For Au clusters vapor-deposited on crystalline titania, oxygen vacancy defects in the titania support stabilize the Au nanoparticles [46], and DFT studies also indicate that oxygen vacancies dictate the dispersion and shape of the Au clusters on titania [35].

In the work reported here, vapor-deposited Au clusters on $TiO_2(110)$ exhibit activity for oxidation of methanol to formaldehyde, as studied by temperature programmed desorption experiments in ultrahigh vacuum. Investigations on these model systems provide valuable insight into understanding the mechanism of oxidation reactions on the Au–titania systems. Methanol is used as a probe molecule because the reaction of methanol on titania single-crystal surfaces, crystalline films and powders has been well studied [64–68]. In addition, the chemistry of methanol on bulk Au surfaces and other noble metals like Cu and Ag have been investigated in detail [69–76], given that Cu and Ag comprise the industrial catalysts used in oxidation of methanol to formaldehyde [69]. Furthermore, the partial oxidation of alcohols is a reaction of considerable industrial importance because these chemical processes are used in the production of commodity chemicals, as well as starting materials for many organic synthesis reactions [77]. Understanding the catalytic oxidation of methanol is also critical for the development of direct methanol fuel cells [78]. In the reaction of methanol on Au clusters on TiO_2 (Au/TiO_2), both Au and titania sites are necessary. Isotopic labeling experiments involving CD_3OH and the incorporation of ^{18}O into the TiO_2 lattice illustrate that the role of the titania support is to initiate the reaction by facilitating O – H bond scission in methanol, and lattice oxygen is incorporated into water that desorbs from the surface. The role of the Au sites is to remove surface hydrogen as H_2, thus preventing recombination of methoxy and surface hydrogen and allowing methoxy to produce formaldehyde at higher temperatures. The dependence of formaldehyde yield on Au coverage suggests that the reaction occurs at Au–titania interfacial sites.

2. Experimental methods

Experiments were performed in two ultrahigh vacuum chambers with base pressures of $\leq 6 \times 10^{-11}$ Torr. Temperature programmed desorption (TPD) experiments were carried out in the first chamber, which was equipped with a shielded quadrupole mass spectrometer (Hiden HAL 301/3F), a cylindrical mirror analyzer for Auger electron spectroscopy (Omicron, CMA 150) and low energy electron diffraction options (Specs) [79–81]. STM and XPS experiments were conducted in the second chamber, which has a variable-temperature STM (Omicron, VT-25), a hemispherical analyzer for XPS experiments (Omicron, EA125), as well as a LEED/Auger system (Omicron, SPEC3) and a quadrupole mass spectrometer (Leybold Inficon Transpector 2) [81–84]. Both chambers have been previously described in greater detail [79–84].

The TiO_2 crystals (1 cm × 1 cm × 0.1 cm, Princeton Scientific Corporation) were mounted on a Ta backplate, which was heated by electron bombardment [80,85]. The temperatures were measured with either a type C or K thermocouple, which was spot welded to the backplate and calibrated with an infrared pyrometer [82]. The crystals were cleaned by several cycles of Ar ion sputtering (20 min, 1 kV, 2–4 μA current to the crystal) followed by annealing for 1–3 min at temperatures above 950 K. The cleanliness and order of the $TiO_2(110)$-(1×1) surfaces were confirmed using a combination of STM, LEED, AES and XPS.

In the first chamber, Au was deposited at room temperature at a rate of 0.1 ML/min from a pure Au pellet (Alfa Aesar, 99.9995%) housed inside a resistively heated W wire cage. In the second chamber, Au was deposited at room temperature using a commercial evaporator (Oxford Applied Research, EGC04) from a Au pellet in a Mo crucible; the sample was biased at +800 V during deposition to repel high energy Au ions. The Au deposition rates were established with an independently calibrated quartz crystal microbalance (Inficon) [84], and 1 ML of Au is defined with respect to the packing density of the Au(111) surface (1.40×10^{15} atoms/cm^2).

CH_3OH (Sigma-Aldrich, 99.93%) and CD_3OH (Cambridge Isotope Laboratories, 99.5%) were purified by several freeze–pump–thaw cycles before use. Oxygen (O_2, Matheson, 99.997%) and $^{18}O_2$ (Sigma Aldrich, 97%) were used as received. The surface was exposed to all adsorbate gases using a stainless steel directed dosing tube [83], which was positioned 2 mm from the face of the crystal, so that the local pressure at the surface was higher than the background chamber pressure and dosing onto the sample holder could be minimized. For the TPD experiments, the surface was exposed to methanol at 100 K and a pressure of 1.5×10^{-11} Torr above the base pressure for 7 s, and this resulted in a saturation exposure, based on the desorption of methanol multilayers in the TPD experiments. For the XPS experiments, the surface was exposed to a saturation dose of methanol at room temperature ($\Delta P=$

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