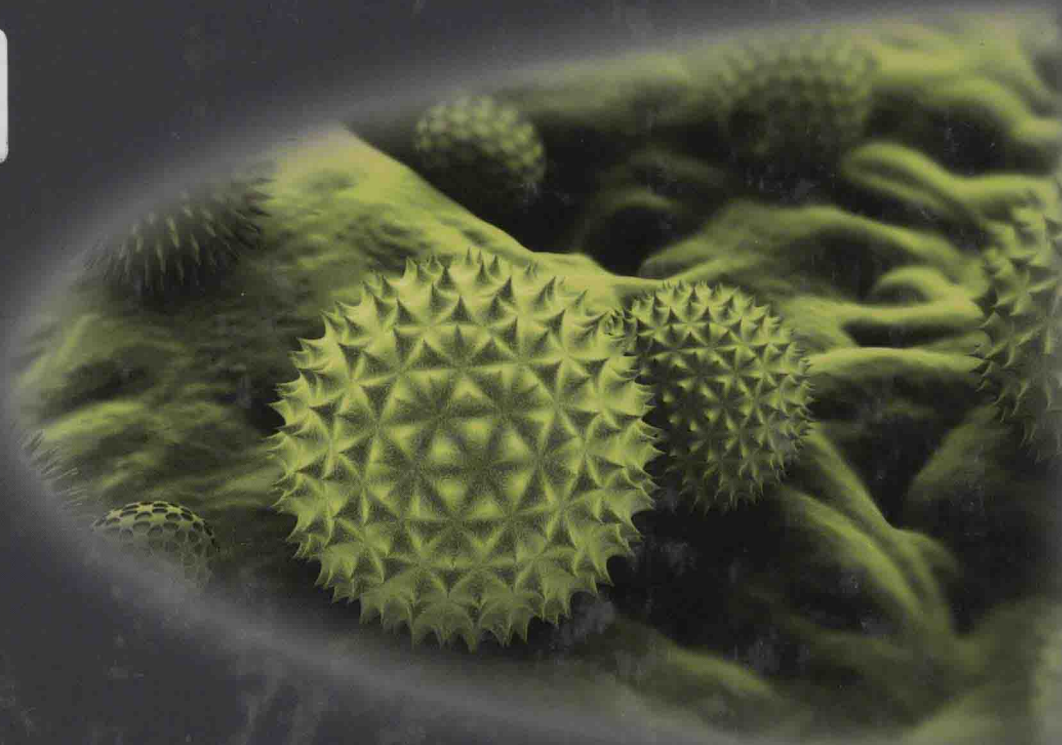


Steven L. Suib  
Editor



# New and Future Developments in Catalysis

Catalysis by Nanoparticles

# NEW AND FUTURE DEVELOPMENTS IN CATALYSIS

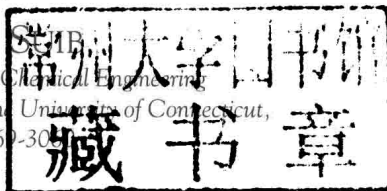
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## CATALYSIS BY NANOPARTICLES

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# Introduction

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Studies of nano-size particles have been the rage for the past 10–15 years. Effects of nano-size particles in catalysis have been known for quite some time, with multiple examples of the effect of small clusters of metal atoms such as the latent image in the photographic process and in several catalytic reactions. Statements often appear in texts that reactions are catalyzed over small size particles faster than over large particles. However, this depends on whether or not the reactions are structure sensitive and influenced by the size of particles and the types of atoms at the surface or interface or structure insensitive where surface area and the size of particles are not important. This book focuses on nano-size particles that have an influence on catalytic activity, selectivity, and stability.

Nano-size Au-based catalysts are currently being studied for oxidation of CO because they have tremendous activity even at temperatures below 0°C. These systems are summarized as well as their activity in water-gas shift and desulfurization reactions. The morphology of nano-size particles is often important in catalytic reactions and this is the focus of a chapter concerning titania catalysts. The photocatalytic activity of titania and zinc oxide and other materials is well known and these are discussed in several chapters. The use of surface science methods to study such systems is essential and these methods are discussed separately.

Nano-lithography is an important area where catalysis is now making new inroads. Another critical area concerns computational studies of metal oxide particles which is relevant in catalysis as well as a variety of other

areas. Nano-size particles have been used in biomass conversion and several chapters concern this area. Various reactions catalyzed by nano-size particles are summarized such as hydrogenation and in reactions important in the medicinal field. A related chapter concerns thin enzyme films on nano-size particles and on electrodes for use in sensing applications for biomedical applications. The use of nano-size particles as mimics of enzymes is also the subject of a chapter. Nano-size particles are also important in electrochemical devices like fuel cells and this area is also discussed.

This book discusses modern synthetic methods used to make nano-size particles. Several methods are detailed about how to stabilize these particles that are used under a variety of atmospheres and thermal environments. Clever methods of attachment of nano-size particles to a variety of substrates are given. The best methods of characterization of such systems are also outlined by several authors. Finally, the use of nano-size particles in a plethora of catalytic reactions is summarized and clearly this field is continually being developed with novel syntheses, characterization methods, and applications. Nanoparticle catalysts and their use in catalytic processes are areas that will continue to grow through the future, as new methods of synthesis and characterization are more fully developed. A specific example is the recent emphasis on the use of atomic layer deposition methods to prepare lithographic-type structures with precise deposition of active components and supports that show excellent activity and selectivity.

## Acknowledgments

SLS thanks the US Department of Energy Basic Energy Sciences Program and Dr. Raul Miranda as well as Dr. Maria Burka of the National Science Foundation, CBET Program for significant ideas about this book and their support of catalysis research.

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# Gold-Based Catalysts for CO Oxidation, the Water-Gas Shift, and Desulfurization Processes

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## 1.1 INTRODUCTION

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Recently, gold has become the subject of a lot of attention due to its unusual catalytic properties when dispersed on some oxide and carbide supports [1–11]. Bulk metallic gold is a very poor agent for the activation of molecules typically used in catalysis ( $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{CO}$ ,  $\text{C}_2\text{H}_4$ , etc.) [12,13], but atomic or molecular species bonded to low-index single crystal gold surfaces are chemically active [14–16]. Among the transition metals, gold is by far the least reactive and is often referred to as a “coinage metal.” In valence photoemission spectra for metallic gold [17], states with Au 6s,p character appear from 0 to 2 eV, while the Au 5d states extend from 2 to 8 eV. The low reactivity of metallic Au is a consequence of combining a deep-lying valence 5d band and very diffuse valence 6s,p orbitals [12,17].

Many experimental and theoretical studies have been focused on understanding the high catalytic activity of gold nanoparticles supported on oxides and carbides [1–11,18]. Quantum effects related to the small size of the particles could be responsible for the enhancement in catalytic activity with respect to bulk gold, but it is becoming more and more clear that interactions between the gold nanoparticles and the oxide or carbide support play a very important role [10a,10d,11,18]. The edge and corner sites of a gold nanoparticle (i.e., sites which have three to four metal atom neighbors) can bond well adsorbates like  $\text{CO}$ ,  $\text{O}_2$ , and  $\text{SO}_2$ . They can even perform the catalytic oxidation of  $\text{CO}$ , but for more demanding reactions the

chemical activity of the isolated Au nanoparticles is not enough. A comparison of the  $\text{DeSO}_x$  activity for the Au/TiO<sub>2</sub>(110), Au/MgO(100), Au/TiC(001) surfaces illustrates the important role played by gold ↔ substrate interactions. The TiO<sub>2</sub> and TiC supports are not simple spectators [11].

The next section of the chapter will discuss fundamental studies examining the bonding interactions of gold with metal oxide and carbide surfaces. Then, we will focus on the use of gold-based catalysts in CO oxidation, the water-gas shift, and the destruction of SO<sub>2</sub>.

## 1.2 BONDING INTERACTIONS BETWEEN GOLD AND METAL OXIDE OR CARBIDE SURFACES

Results of scanning tunneling microscopy (STM) and transmission electron microscopy (TEM) indicate that Au grows on most metal oxide surfaces forming three-dimensional (3D) particles [2b,10d,19]. For example, at 300 K, Au clusters nucleate mainly on step sites or on defect sites present in the terraces of TiO<sub>2</sub>(110) [2b,20,21]. The interaction of Au with an ideally flat TiO<sub>2</sub>(110) surface is quite weak [22], and a substantial amount of particle sintering occurs when the system is annealed from 25 to 600 K [2d,19]. In general, density functional (DF) calculations for the adsorption of Au atoms on MgO(001) and TiO<sub>2</sub>(110) give bonding energies below 0.5 eV [4,6,8a,10]. Only in the presence of O vacancies strong bonding interactions are seen between Au and the oxide surfaces [8a,10,22]. On the O vacancies, an oxide → Au charge transfer takes place [8a,10]. Studies of scanning tunneling spectroscopy (STS) indicate that the Au clusters supported on TiO<sub>2</sub>(110) have a small band gap (0.2–0.6 V) and electronic properties different from those of bulk metallic Au [2b]. This is important, since such a difference could be responsible for the variation in chemical activity when going from the nanoparticles to bulk gold [2b].

What happens when Au is deposited on a substrate which has physical and chemical properties different from those of an oxide? The carbides of the early-transition metals exhibit, in many aspects, a chemical behavior similar to that of very expensive noble metals (Pt, Pd, Ru, or Rh) [23]. Transition metal carbides exhibit broad and amazing physical and chemical properties [23–25]. Their properties may be viewed as resulting from a combination of those of covalent solids, ionic crystals, and transition metals [23,25–27]. In recent studies [11,18], high-resolution photoemission, STM, and DF calculations were used to study the adsorption of gold on a TiC(001) surface. The Au ↔ TiC(001) interactions were much stronger than typical Au ↔ oxide interactions [18]. For example, the calculated binding energies for an Au atom on TiC(001) and TiO<sub>2</sub>(110) are –1.91 eV [18] and –0.38 eV [8a], respectively. For Au/TiC(001), the photoemission and DF results point to the formation of Au–C bonds [18]. Overall the bond between Au and a TiC(001) surface exhibits very little ionic character, but there is a substantial polarization of electrons around Au [18] which enhances the chemical activity of this metal [11,28,29].

Figure 1.1 displays electron-localization function (ELF) plots for Au<sub>4</sub> on a series of MC(001) (M = Ti, Zr, V, and Mo) [18,30]. In all these systems, there is a substantial concentration of electrons in the region outside the Au<sub>4</sub> unit. A similar phenomenon was observed for Au, Au<sub>2</sub>, and other small clusters containing one layer of gold in contact with the carbide substrates [18,30]. In the case of clusters with two layers of Au, the electron polarization for the second

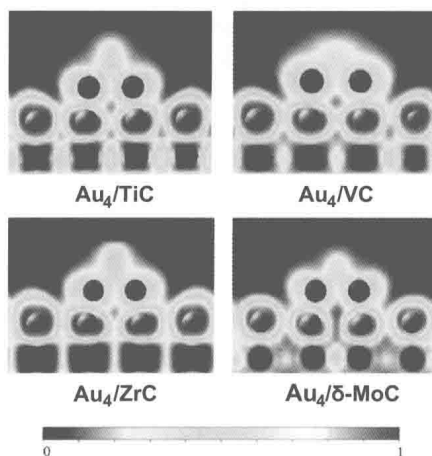


FIGURE 1.1 Calculated electron-polarization plots for a series of  $\text{Au}_4/\text{MC}(001)$  surfaces ( $M = \text{Ti}, \text{VC}, \text{Zr}, \text{Mo}$ ). Taken from Ref. [30], Copyright 2010 American Chemical Society.

layer of atoms was much less pronounced than that seen for the  $\text{Au}_4/\text{MC}(001)$  systems [18,30]. On the basis of the charge polarization induced by the carbide substrates, one can expect big differences between the chemical reactivity of 2D and 3D gold clusters. The  $\text{Au}_4/\text{MC}(001)$  systems should be very active in the bonding of electron acceptor molecules ( $\text{CO}$ ,  $\text{O}_2$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{SO}_2$ , etc.).

### 1.3 OXIDATION OF CARBON MONOXIDE ON Au-OXIDE AND Au-CARBIDE SURFACES

The oxidation of carbon monoxide ( $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$ ) over metal/oxide catalysts is significant for understanding fundamental processes associated with methanol synthesis, the water-gas shift reaction, the reforming of alcohols, the operation of fuel cells, and automotive exhaust controls, to mention a few major applications in the area of catalysis [2,3,6,10,13,22]. In automotive exhaust emission control, the complete oxidation of carbon monoxide is of prime importance to meet increasingly stringent environmental regulations in a practical way [13]. Furthermore, since the classic studies of Langmuir, CO oxidation on metal and oxide surfaces is often viewed as an ideal reaction for fundamental investigations in heterogeneous catalysis [2,3,6,10,13,22]. High surface area  $\text{Au}/\text{TiO}_2$  catalysts are very efficient for the oxidation of CO (6,23) [1,2b,31,32]. The bottom trace in Figure 1.2 shows how the CO oxidation activity of an  $\text{Au}/\text{TiO}_2(110)$  surface changes as a function of Au coverage [33]. A maximum activity is found for an Au coverage of  $\sim 0.3$  monolayer (ML). When these activity data are put together with STM results [2b,32], one finds that there is a marked size effect on the catalytic activity, with Au clusters in the range of 3–4 nm exhibiting the maximum reactivity. For this size, most of the particles have a band gap of 0.2–0.6 V according to scanning tunneling spectroscopy (STS) [2b]. Particles with a larger band gap ( $>1$  V) display a lower reactivity, and particles with metallic character (band gap  $\sim 0$  V) are the least active. Thus, there is a correlation



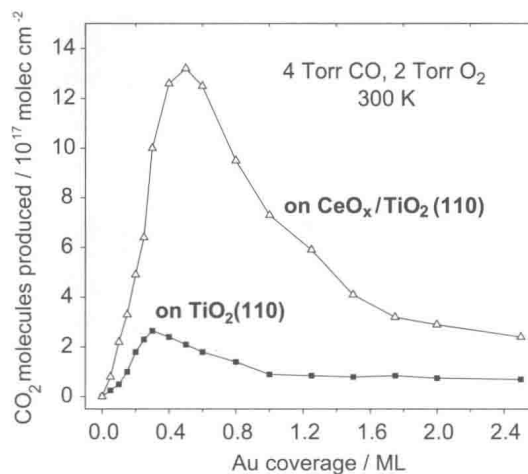


FIGURE 1.2 Oxidation of CO on Au/TiO<sub>2</sub>(110) and Au/CeO<sub>x</sub>/TiO<sub>2</sub>(110) surfaces as a function of Au coverage. In the case of Au/CeO<sub>x</sub>/TiO<sub>2</sub>(110), ~12% of the titania surface was covered with ceria. Taken from Ref. [33], Copyright 2009 National Academy of Sciences USA.

between the electronic and chemical properties of the supported Au nanoparticles. Studies of STM indicate that exposure to CO has no effect on the morphology of the Au/TiO<sub>2</sub>(110) surface [2b]. On the other hand, significant morphological changes occur after exposure to O<sub>2</sub> or CO:O<sub>2</sub> mixtures. In these cases, the Au cluster density is greatly reduced as a result of sintering [2b]. This sintering eventually leads to a decrease in the CO oxidation activity of the Au/TiO<sub>2</sub>(110) systems.

In recent studies, the CO oxidation on Au/TiO<sub>2</sub> catalysts occurs on metal sites at the gold-oxide interface [32,34]. Infrared-kinetic measurements indicate that O—O bond scission is activated by the formation of a CO—O<sub>2</sub> complex at dual Ti—Au sites at the Au/TiO<sub>2</sub> interface. DF, which provides the activation barriers for the formation and bond scission of the CO—O<sub>2</sub> complex, confirms this model. The observation of sequential delivery and reaction of CO first from TiO<sub>2</sub> sites and then from Au sites indicates that catalytic activity occurs at the perimeter of Au nanoparticles [32,34].

The catalytic activity of Au—TiO<sub>2</sub> can be improved by the addition of ceria [33,35]. The ceria helps with the dispersion on the gold enhancing the rate of CO oxidation. Figure 1.3 shows an STM image acquired after depositing Ce on TiO<sub>2</sub>(110) under an atmosphere of O<sub>2</sub> [33]. Most of the spots (~70%, labeled “a”) have a height of  $1.3 \pm 0.2 \text{ \AA}$  and correspond to small wires of CeO<sub>x</sub> [33]. A minority of the spots (~30%, labeled “b”) have a height of  $1.9 \pm 0.3 \text{ \AA}$  and probably correspond to (1 × 2) reconstructions of TiO<sub>2</sub>(110) induced by O<sub>2</sub> chemisorption [33,36,37]. Figure 1.3b displays an STM image taken after depositing ~0.25 ML of Au on the CeO<sub>x</sub>/TiO<sub>2</sub>(110) surface of Figure 1.3a. The deposition of Au was done at room temperature. One can see particles of Au that were simultaneously located on “a” and “b” sites. When STM images for the Au/CeO<sub>x</sub>/TiO<sub>2</sub>(110) system are compared to those collected for plain Au/TiO<sub>2</sub>(110) [2b], the presence of ceria favors the dispersion of the gold on the titania terraces and the metal particles are not located mainly at steps of the surface as it happens in the case