CHAPTER 2

Catalysis by Metallic Nanoparticles: Shape and Size Dependency

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CONTENTS

1. INTRODUCTION

Metallic nanoparticles, especially those of Au (and to some extent those of Ag, Cu, and others) exhibit remarkable catalytic properties usually attributed to their high surface-to-volume ratio. Au nanoparticles or "nanogold" have been reported to promote a variety of catalytic reactions, including oxidation reactions, notably even under ambient conditions [1, 2]. These observations have given rise to great anxiety and excitement and to a new awakening since bulk Au has been conventionally considered and proved to be inactive for catalysis, due to various reasons, including its high value of ionization potential. The reasons for this observed unusual reactivity of gold nanoparticles have been postulated and these aspects have given rise to a branch of science called "Au catalysis," as revealed from the numerous publications in this area in recent times. Several reviews have appeared in the literature, focusing on the importance of Au nanoparticles in catalysis [3–11]. There are various reasons for this interest in catalysis via Au nanoparticles, including the possibility of its relevance to fuel cell applications—especially, how does an inactive metal like Au become active in the nanostate and how does it promote the selective oxidation of CO in the presence of H_2, a reaction of relevance for the development of energy conversion devices such as fuel cells. The central theme in these studies is to establish that Au clusters of specific sizes (say, <55 atoms or in the range of a few nanometers in diameter) and shapes alone are active for observed catalytic activity, more so for the low-temperature oxidation of CO.

The necessity of additives and promoters tends to keep the particle sizes of these clusters, in addition to acting as supports for the effective dispersion of the active phase. In this capacity, the additives have other roles, such as exposing the active component, increasing the reactive surface, and geometrically generating and sustaining the so-called "active sites," in addition to acting as a heat sink. These aspects have been emphasized in various publications in the literature.

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2. WHY GOLD NANOPARTICLES?

It is known in catalysis, ever since the specificity in ammonia synthesis on Fe(111) surfaces was shown to be nearly 600× as active as on other low index planes, namely (100) and (110), that there can be some specificity of the surface planes exposed in catalysis. This has also been manifested in the formulation of demanding and facile reactions, or structure-sensitive and structure-insensitive reactions, respectively, a concept that has been routinely used in this field to classify reactions [15, 16] in the past 3 to 4 decades. In fact, almost all known catalytic reactions have been classified under structure-sensitive or structure-insensitive categories. Therefore, it is not surprising that Au nanoparticles exhibit size and shape specificity in catalysis. If this is so, why are we so concerned with the shape and size specificity of Au for catalysis if this were to be a natural and possibly universal consequence of any catalytic system? At this time, these kinds of philosophical questions have not yet been addressed extensively, but the focus has been to the exploitation of gold nanoparticles for a variety of reactions and one simple compilation [15–39] of the reactions catalyzed by gold nanoparticles is given in Table 1. The reaction types include oxidation [15–28, 37, 38], reduction [21, 29, 30] of organic substrates and CO, hydrochlorination [31, 32], esterification [35, 36], fine chemical synthesis [30], and hydrogenation [39].

From a density functional theory (DFT) study of the clusters of Au, Sankaran and Viswanathan [40] postulated that, in the case of Au, only particular sizes of its nanoparticles possess spatial orientation and symmetrically allowed orbitals and thus the corresponding eigenvalues that are appropriate for interaction with the incoming adsorbate molecules that undergo transformations on the surface. For other sizes of nanoparticles the frontier wave functions have predominant character and hence there are no spatial orientations or eigenvalues that would facilitate the transformation of the former clusters. Due to these spatially oriented eigenfunctions, the Au clusters interacted with the support and the reactant system exhibit altered activity. The authors argued that only certain sizes of clusters have wave functions suitable for interaction with the substrate molecules. In this connection they quote $(Au)_x$ system as one of the active clusters. A similar conclusion was also drawn by Pulido in his presentation [41]. The data generated by Sankaran and Viswanathan [40] on the nature of frontier wave functions of the clusters of varying sizes are reproduced in Figure 1.

Table 1. Typical reactions catalyzed by Au nanoparticles.

S. No.	Reaction	Refs.
1	Alcohol oxidation	[15–17]
2	Oxidation of glucose and hexoses	[18–21]
3	Oxidation of CO	[22–24]
4	Oxidation of glycerol	[25, 26]
5	Oxidation of styrene, ethylbenzene, allylic oxidation	[27, 28]
6	Reduction of nitrophenols	[21, 29, 30]
7	Hydro-chlorination of ethylene	[31, 32]
8	Hydrogenation of alkyne	[33]
9	Gluconic acid from glucose	[34]
10	Methyl glycolate from ethylene glycol	[35]
11	Vinyl acetate monomer from ethylene, acetic acid, and oxygen	[36]
12	CO electro-oxidation	[37]
13	Fine chemical synthesis	[30]
14	Oxidation of propylene to propylene oxide	[38]
15	Alkene and arene hydrogenation	[39]

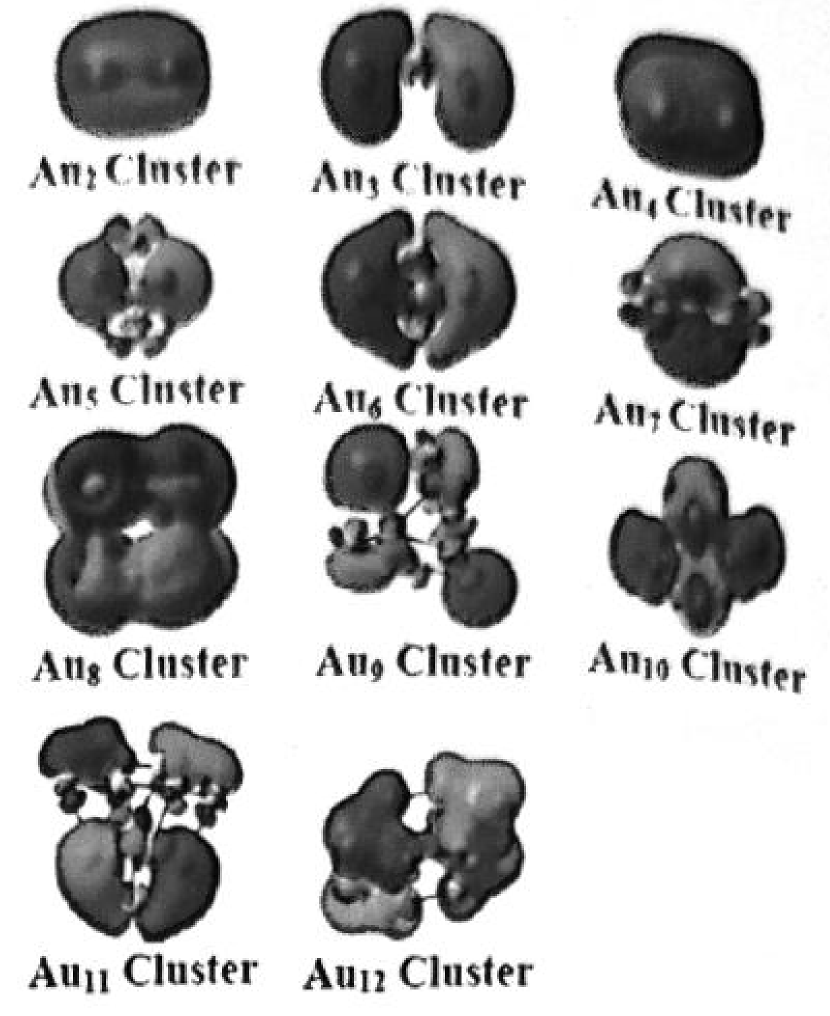

Figure 1. The frontier wavefunction contours for various Au clusters $(Au)_n$, where n = 2–12. Reproduced with permission from [40]. M. Sankaran and B. Viswanathan, *Bull. Catal. Soc. Ind.* 5, 26 (2006). © 2006, Bulletin of Catalysis Society of India by Catalysis Society of India.

A more comprehensive study has been published by Visikovskiy et al. [17], with clusters varying in size, containing number of Au atoms n_A in the range $11 < n_A < 1600$. They showed that the d-band parameters as well as the binding energy of Au $4f$ core levels undergo drastic changes for 2.6-nm-diameter nanoparticlesor $n_A < 150$ atoms. The smaller number of wave functions of valence electrons undergo effective hybridization (like in molecular systems) and hence results in narrowing the d-band width. These effects can be reflected in the shift of the d-band center with respect to the Fermi level (the concept of the position of d-band center has some consequence in catalysis and has been recognized in earlier literature). Even though the authors recognize certain limitations in their calculations of the parameters, they believe that the results provide "prominent insight into dramatic changes of the d band parameters of gold nanoclusters," and that the d-band parameters like the width and the spin–orbit splitting possibly scale almost linearly with the average coordination number of the clusters.

Other DFT calculations by Fenger et al. [42] have shown that adsorption of the molecule to the Au cluster is accompanied by a significant charge transfer from the surface to the N atom of the reactant nitrophenol molecule for its reduction to aminophenol. It may be presumed that the message from this study is that Au clusters possibly behave more like molecular systems rather than like bulk surfaces. This point has not yet come out explicitly in the literature but one can hope that this will be the destination of the research efforts. Lin et al. [18] have also examined the reduction of p-nitrophenol with $NaBH_4$ on Au clusters supported on alumina (Al_2O_3). Their main contention is that the catalytic

Table 2. Au nanoparticle size and the corresponding turnover frequency for the 4-nitrophenol reduction (reaction time is fixed at 60 s).

Particle size of the Au nanoparticle [nm]	Conversion [%]	Turnover frequency [mol g^{-1} s^{-1}]
1.7	73.0	1.83×10^{-2}
3.4	82.5	2.06×10^{-2}
5.7	71.3	1.78×10^{-2}
8.2	62.3	1.56×10^{-2}

Source: Reproduced and adopted from [18], C. Lin et al., *Molecules* 18, 12609 (2013). Permission not required due to open access policy of the publisher.

activity depended on the size of the Au nanoparticle, the activity being highest when the average size of the cluster is ~3.4 nm. The essence of their results is given in Table 2.

In another detailed study, Landman et al., have claimed in a combined experimental and first-principles quantum-mechanical calculations and simulation formulation of the detailed mechanism, that the barrier for the various steps, especially for the interaction of adsorbed CO and adsorbed oxygen and that for the desorption of product CO_2 are considerably reduced for a 20-atom Au cluster on MgO surface. Alves et al. [44] have considered the activation and dissociation of molecular O_2 on Au nanoparticles of size ~1 nm. They have shown that surface Au oxidation is energetically favorable when the nanoparticle size is ~1 nm. It therefore appears that cluster size, cluster support interaction, defects in support, charge state of the cluster, the dimensionality of the active cluster, and other parameters are responsible for the reactivity of the cluster. This aspect has been repeatedly emphasized in the literature.

3. CATALYSIS BY GOLD NANOPARTICLES

It is generally believed that catalytic reactions experience a reduced energy barrier route for transformations and these alternate routes in the potential energy surfaces could have arisen due to the nanostate of the catalytic particles. The reactivity of the nanostate has been realized for at least a century in practical systems although it might have been known for many centuries as a feature in living beings. This realization has not been explicitly stated in the literature of that period even though it has been in the minds of catalyst scientists all through, since they did not have direct experimental proof for want of the appropriate resolution with the microscopes available then. This situation has given rise to many issues in the minds of the interested readers. They are

- If shape and size have been identified as responsible for the observed selectivity in catalysis and if this is already known, then why is this important for catalysis for Au nanoparticles?
- Small nanoparticles of metals such as Au bind strongly to supports such as TiO_2 and FeO, which are generally observed to be more effective in making Au nanoparticles active in catalysis than supports such as MgO. What is the specific reason for this observation? [45]
- The thermodynamic stability of adsorbed intermediates for catalytic reactions can either increase or decrease with decreasing metal nanoparticle size below 8 nm, depending on the reactant system. What is the reason for this limit of 8 nm?

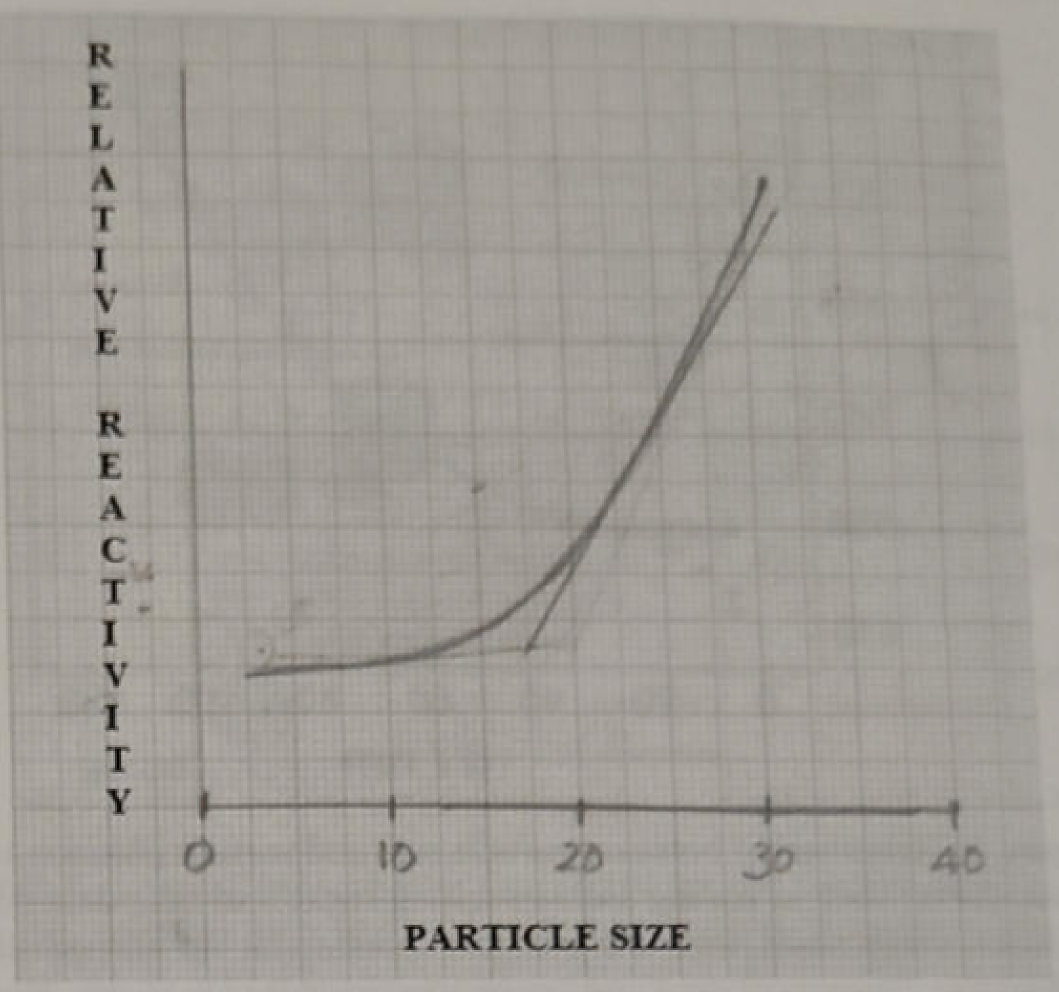

Figure 2. Dependence of reactivity for scaling and nonscaling regions of particle size. Only one particular type of gradient change is shown, but the gradient changes can have both types of slopes. The trend can be either upward or downward as particle size increases.

- There is a scaling region above which particle size is linearly related to reactivity. There is also a certain range where scaling is not obeyed at all. The reasons for these two regions of reactivity have not been explicitly known although they have been identified, as shown in the hypothetical plot in Figure 2.
- The reaction to insert O_2 into the Au–H bond of adsorbed H on the Au (111) surface to make AuOOH ($O_{2,g} + H_{ad} \rightarrow OOH_{ad}$) is exothermic by – 80 kJ mol^{-1}. This adsorbed hydroperoxyl species is thought to be a key intermediate in selective oxidation reactions over Au nanoparticle catalysts, but its production by this reaction may also provide a route for O_2 evolution in possible electrochemical cells.
- Au nanoparticles appear to exhibit strong interactions with the support and hence their reactivity in the supported state is noticeably different from that of the unsupported state. This has been repeatedly observed and recorded in the literature, but deserves much more attention for its significance. See the second point in this list for specific cases.
- There are variety of other aspects of Au nanoparticles that deserve attention, such as plasmon resonance and its dependence on the size and shape of nanoparticles. These aspects will not be considered in this presentation except to quote some essential points from the literature for reference. Haiss et al. [19] have shown that the peak position of plasmon resonance is a function of particle size (see Fig. 3) and also the linear dependence of the absorption ratio ($A_{(spr)}/A_{650}$) as a function of the logarithm of particle size (see Fig. 4) [24].

Although this type of straightforward relationships of the behaviour of Au nanoparticles with particle size have been indicated in some of the published literature, it should be

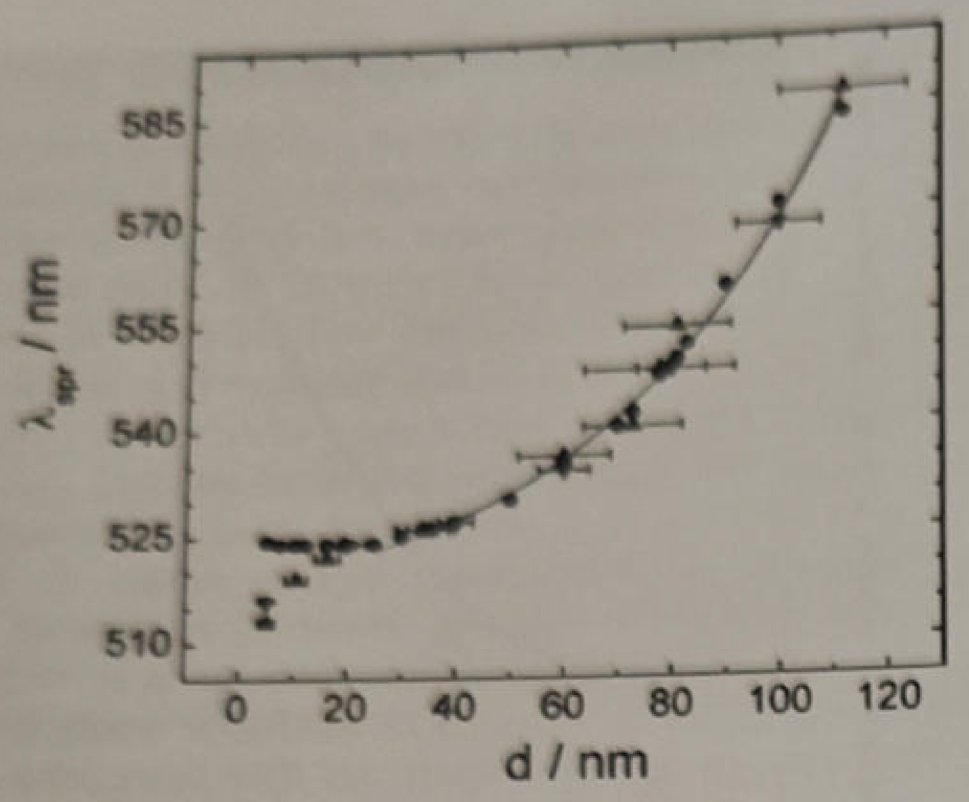

Figure 3. Relationship between particle size and surface plasmon resonance (SPR) both in scaling and nonscaling regions of size; data points triangles, synthesized, inverted triangles commercial Au nanoparticles, dashed line theoretical data and circles are calculated particles. Reproduced with permission from [19], W. Haiss et al., *Anal. Chem.* 79, 4215 (2007). © 2007, American Chemical Society.

emphasized that these relationships are not as straightforward as they appear to be.

A possibly comprehensive study on cluster sizes ranging from 11 to 1600 Au atoms has been reported by Visikovskiy, as stated earlier [17]. They have employed a photoemission technique to monitor the changes of the *d*-band width, $5d_{3/2}$–$5d_{5/2}$ separation and the *d*-band center. They have also recorded steep changes in these parameters when cluster size decreases below 150 atoms, owing to the band narrowing caused by the hybridization of fewer wave functions of the valence electrons when the system tends towards molecular systems. Eliminating the final state effects from the raw data and only considering the initial state parameters for their photoemission measurements, they concluded that the average Au–Au distance is shorter in clusters than for bulk Au. This shortening could have arisen due to effective overlap of the wave functions, whereas in bulk Au this type of directional overlap may not be possible and hence Au–Au distance would be higher in bulk systems.

It has been recognized that localized surface plasmon resonances are central for specific behaviors of nanoparticles and has been shown to be size dependent. This indirectly means that the surface properties that are essential for catalysis can also depend on the surface plasmon resonance [20]. The observation of plasmon resonance in metallic systems has also been exploited for photocatalysis, which has led to the development of the concept of plasmonic catalysis, or plasmon-assisted catalysis, in recent years [46].

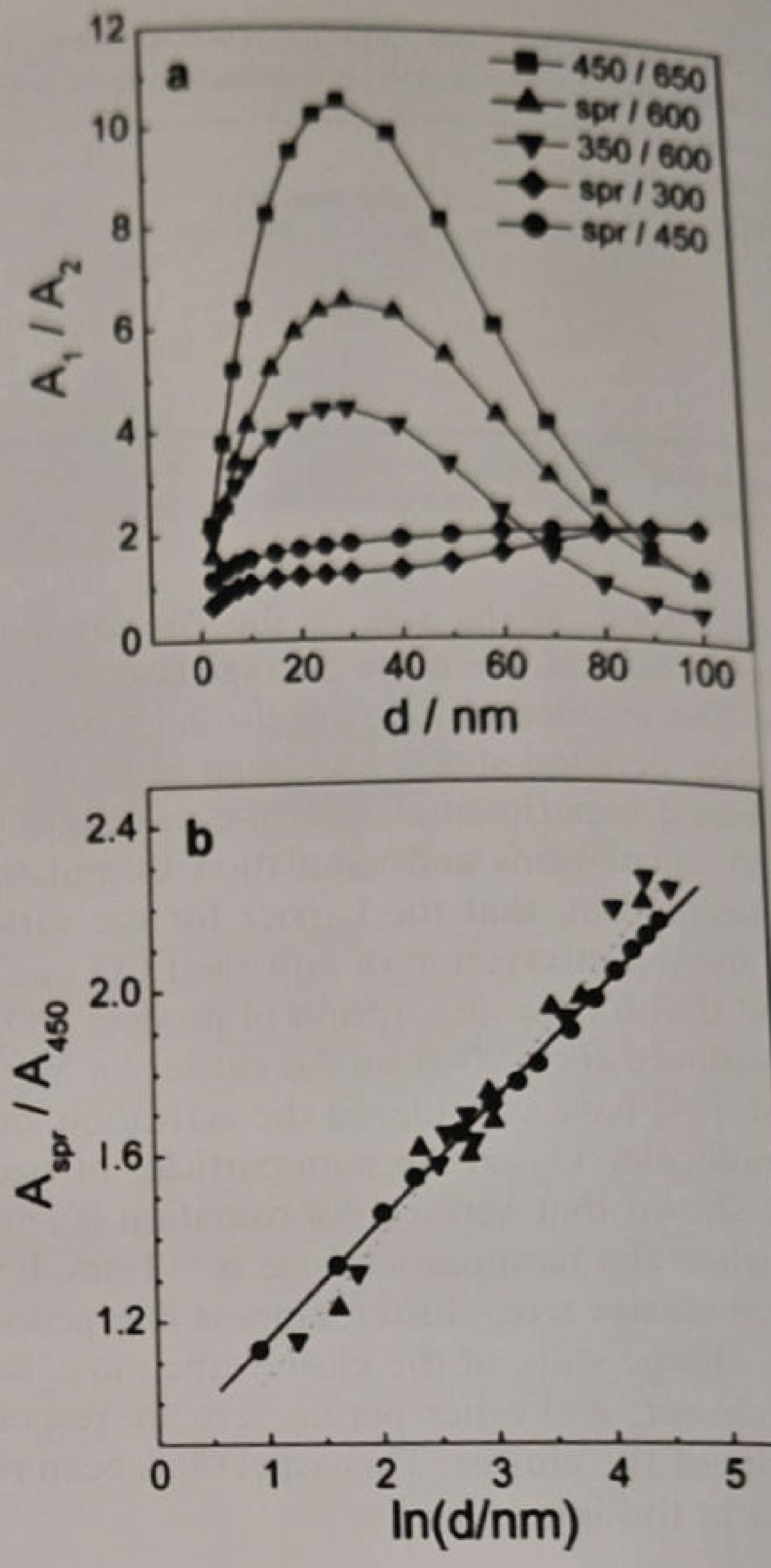

Figure 4. (a) Calculated ratios of absorbance values of Au particles in relation to their diameter (b) Ratio of absorbance of Au nanoparticles the surface plasma resonance peak (A_{SPR} to the absorbance at 450 nm (A_{450} as a function of the logarithm of particle diameter). Reproduced with permission from [19], W. Haiss et al., *Anal. Chem.* 79, 4215 (2007). © 2007, American Chemical Society.

3.1. Support Effect on the Activity of Gold Nanoparticles

There is one aspect of Au catalysis that has been given considerable attention with no single postulate emerging as the reason for the reactivity of supported Au nanoparticles. It is generally conceived that there can be two kinds of interactions between the active metallic species and the support, namely an electronic effect where charge transfer to or from Au nanoparticles is envisaged as a possible reason for the altered activity observed with supported nanoparticles. A variation on this same postulate has been seen in the creation of oxygen vacancies in the support with geometrical disposition or geometrical regularity. In addition, the phase composition of supports (such as brookite or anatase in the case of TiO_2) has also been shown to have an influence on the observed catalytic behavior of nanoparticles. The supports can also facilitate the shape and geometry of the nanoparticles formed on it. This has been recognized with the terminology decoration of the active phase in the field of catalysis. Although the electronic and geometric factors responsible for metal support interaction have been known in the literature for several decades, it is still not clear which one is really responsible for the supported system to exhibit altered normalized activity. However, it is necessary to consider additional aspects for the reactivity of supported Au nanoparticles. There are a few aspects on which clarity may be required in the near future:

- Does the support sustain the integrity of the nanoparticles without allowing them to agglomerate?
- Does the support facilitate the formation of specific shapes of the nanoparticles of Au?

- Does the support partially cover the nanoparticles and thereby stabilize the hemispherical geometry of the nanoparticle?
- Does the interaction between the support and the active phase induce the generation and sustaining of the new or otherwise active sites that are responsible for the observed catalytic activity?
- The support/nanoparticle interface may give rise to specific active sites that may facilitate some catalytic reactions, for example in the oxidation reactions; these interface sites may facilitate the oxygen release involved in the partial oxidation reaction. This aspect has not so far been addressed adequately in the literature.
- The interface sites between the support and the active nanoparticle can facilitate the activation of the substrate molecule. It is also possible that the transformation or required rearrangement in the reactant molecule (the so-called intermediates or activated state) may be formed on these interface sites in a facile manner.
- Although the nature of the support (e.g., oxides, carbides, nitrides) has always been considered, no consensus view has emerged on whether the surface group's functionality or the bulk electronic behavior is responsible for the support–metal interaction in these systems. Cuenya [21] has expressed this concern by stating that "by now one cannot simply neglect nanoparticle support interaction especially when a thorough understanding of the origin of the catalytic reactivity of the supported nanoparticles is desired."

Landman et al. [43] have considered the oxidation of CO on Au in the nonscalable regime and concluded the factors responsible for the altered activity are "the role of the metal oxide support and the defects in them, the charge state of the cluster, structural functionality of the cluster, electronic size effects the chemical reactivity of the metal clusters adsorbed on the support." It is therefore necessary to assume that not one single factor appears to be responsible for the altered activity of Au nanoparticles. It is possible that the presently available information restricts one from outlining the one single reason for this altered activity of Au nanoparticles. Turner et al. [22] have reported that nanoparticles of Au with sizes <2 nm (or a cluster of 55 atoms) alone are active for the selective oxidation of styrene with O_2, which has been attributed to the altered electronic structure intrinsic to small nanoparticles.

3.2. Insights Into Catalysis by Gold Nanoparticles

The search for reactivity differences with cluster size of Au nanoparticles has not yet led to a fixed value or even a narrow range of values at which the reactivity shows a maximum. Choudhary and Goodman [8] showed that cluster sizes in the range of 3–4 nm exhibit maximum activity for CO oxidation. Fenger et al. [42] have shown that particles sizes in the range of 10–15 nm exhibit highest rates for borohydride reduction of *p*-nitophenol to *p*-aminophenol. Geng and Lu [47] showed that Au nanoparticles of sizes 2–6 nm were more active than large-sized particles (12–41 nm) for the oxidation of CO in alkaline medium. Landman et al. [43] have considered reactivity differences between variously sized nanoparticles from the correlation diagram of local density of states (LDoS) and showed that the wave functions of Au_4 (narrow *d*-band) cluster give rise to weak binding with oxygen on top mode due to lack of overlap between *d*-states of the cluster and molecular states of oxygen. Their results are shown in Figure 5.

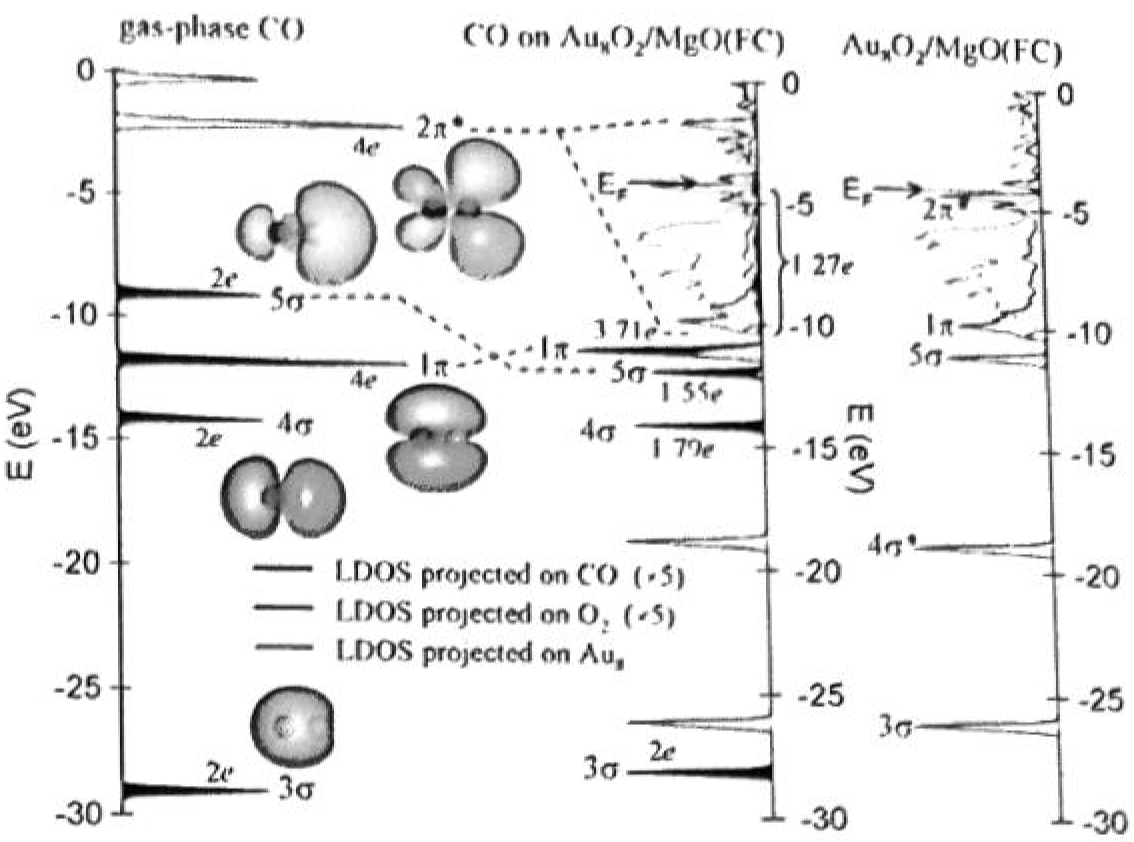

Figure 5. Local density of states projected on the orbitals of CO, O_2, and Au_8 together with that of free CO, to indicate how these clusters are specific in activating the wave functions of the reactant molecule.

It can be seen from this figure how the frontier orbitals of CO, i.e., 5σ, 1π, and 2π, are perturbed on adsorption onto Au (Au_8) cluster, and the oxygen also is capable of interacting with the same cluster, which is shown in the right side of the figure. Goodman [25] has carried out surface science studies on model systems to understand the enhanced catalytic activities of nanosized metal clusters. He has observed a correlation between cluster size, morphology, and electronic properties with catalytic activity. Ringe et al. [20] have studied the size-dependent plasmonic properties of nanoparticles and concluded that the distance along which the oscillation occurs is important for the plasmon resonance and not the intrinsic shape of the nanoparticle. However, it is not clear if this postulate can be extended to the catalytic activity also. The catalytic behavior of nanoparticles is dependent on the nature of active sites generated and these can be different for different shapes of nanoparticles especially due to the fact the coordinative unsaturation of the sites may be dependent on the shape of the particle [48–53]. The size and shape of nanoparticles are not the thermodynamically stable state and hence they can undergo reconstruction under the influence of process parameters or interaction with the reacting molecules. This situation may be particularly applicable to Au nanoparticles. The effect of the size of Au nanoparticles on the observed catalytic reactivity can still be considered to be an open question. The essential observations leading to this state of affairs are:

- The quantum size effects generated by the electrons confined in a small volume.
- The changes in conducting behavior, especially the transition from semiconducting to metallic behavior, as function of particle size.

- The changes to higher binding energy (nearly 0.8 eV for Au nanoparticles of 1.9-nm size) with respect to pure Au ($4f_{7/2}$) due possibly to initial state effects as well as to the positive charge left in the system after photoionization (final state effects).
- The specificity of special planes for reactivity has been established and has been identified as roughness of the surface.
- The possibility of existence of energetically favorable isomers, which could also be associated with the phenomenon of reconstruction.
- The underlying support can interact with the active phase and therefore can induce generation of so-called new active sites.
- The $\sim 1/d^3$ scaling law (where d is the size of the nanoparticle) for activity has also been proposed in the literature.
- It is therefore clear that the reactivity of Au nanoparticles cannot be associated with a single governing parameter, while in the case of other metallic nanoparticles a single or consistent group of parameters could be assigned for the activity alterations observed.

3.3. Shape Effects

One can expect that the shapes of nanoparticles can influence the observed catalytic properties. However in the case of Au nanoparticles the only established observation is that the hemispherical particles are better performing for CO oxidation than are spherical particles. The dependence of shape of nanoparticles on reactivity has been possibly shown for Ag and Pt nanoparticles and not to the same extent on Au nanoparticles.

3.4. Comparison of Gold and Silver Nanoparticles

Like Au nanoparticles, nanosized Ag catalysts have also attracted attention because of their unique catalytic properties for various reactions, in particular for CO oxidation at low temperatures, because they exhibit high catalytic activity and stability at ambient conditions. Like Au nanoparticles, the Ag system also is influenced by factors such as support, pretreatment conditions, and the presence of a second component. Recently, Zhang et al. [54] examined the oxidation activity of Ag nanoparticles and came to three main conclusions:

(1) the catalytic activity of Ag nanoparticles showed dependence on the size of the particles;
(2) the reactivity of Ag nanoparticles is dependent on the nature of pretreatments, the support, and other factors; and
(3) the oxidation reaction is dependent on the nature of sites that can be generated at the interface and of the surface and subsurface species formed in the Ag nanoparticles.

It is equally true for Au nanoparticles. However, the charge and species transfer are essential factors for the observed catalytic behavior of Ag and Au nanoparticles and details of these two aspects are still absent for these two composite systems (a model is shown in Fig. 6).

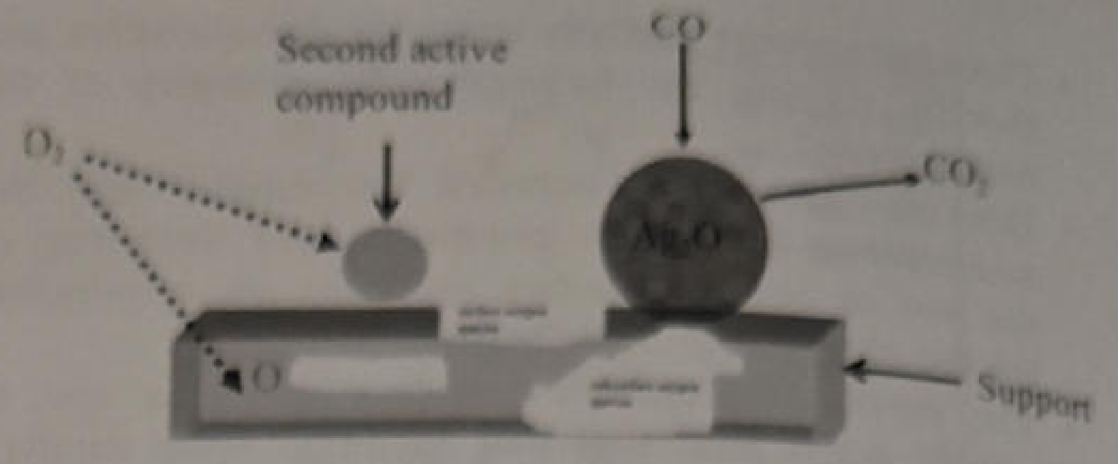

Figure 6. A conceptual framework for CO oxidation on supported metallic nanoparticles. Adopted from [23], M. H. Rashid and T. K. Mandal, *Adv. Funct. Mater.* 18, 2261 (2008). © 2008, Elsevier.

4. PERCEPTION

The motivation for this chapter was not to summarize all the results reported in literature. In fact, the omission is far more than the selection. It is also not claimed that those selected are the most appropriate. The sole aim in this presentation is to point out that there are some special features of the wave functions of Au nanoparticles of particular size and shape and these features are not simply altered with the number of Au atoms found in Au nanoparticles. Only certain numbers of Au atoms provide specific geometry and active sites, possibly because of the participation of $4f$ and $5d$ orbitals of Au atoms. It is hoped that the special features of these wave functions with respect to Au nanoclusters will be soon identified and the specificity of catalysis by Au nanoparticles will be rationalized.

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ABBREVIATIONS

CO	Carbon monoxide
DFT	Density functional theory
MgO	Magnesium oxide.

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