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# Investigating the effect of gold-palladium bimetallic nanoparticles on TiO2 and the catalytic activity in CO oxidation

**Ntholeng, Nthabiseng**

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# Chapter 1

## Literature Review

## 1.1. Introduction

Gold is unique compared to other metals of group 11 (IB) [1]. In the bulk state it shows exceptional chemical properties such as its resistance to oxidation and corrosion [1]. However, it has long being neglected as a catalyst because in the bulk state it does not adsorb reactive molecules such as CO and $H_2$ very well. Therefore it was thought to be inert when compared to the traditional Platinum Group Metals (PGM) such as Pt, Pd and Rh [2-4]. The reason for this conclusion was solely based on the fact that gold metal has fully filled d shell. This notion was overturned by the work of Masatake Haruta in the mid 1980's [5-6]. Haruta's discovery showed for the first time that gold was surprisingly an active catalyst, provided that specific preparation requirements are met. He showed that producing hemispherically attached Au particles of size 1- nm is essential for obtaining high catalytic activity [6]. It is this finding that gave rise to a number of exciting aspects of catalysis by gold that is currently still attracting academic investigations and industries. The key factor to these findings is that gold is highly active when supported in nanoparticulate size on metal oxides. It is also believed that "inert gold" is converted into a highly active catalyst by reduced dimensions and a strong interaction of Au with the support [7]. The reduced dimensions introduce discrete electronic structures, modified physical structures and altered chemical reactivities [8].

The most studied reaction as a model reaction for gold catalysis has historically been CO oxidation at low temperature because of its potential applications and serves as a platform to understand other gold-catalyzed complex reactions. Carbon monoxide oxidation is quite a simple reaction that can reveal preparation, composition and structure of gold catalysts and can be used as a measure of their activity [9]. The unique and useful properties of nano-gold have generated tremendous interest amongst researchers.

However, the quantum effects introduced by reduced dimensions results in melting points of nano-gold metal: as low as 573 K [10]. A detrimental result of this lowered melting point is that

the gold nano-particles sinter much more readily when compared to Pt and Pd nanoparticles when calcined at temperatures above 573 K [10]. Such gold catalysts are therefore not ideal for operating under harsh conditions, particularly high temperatures. Therefore, these limit potential applications of gold catalysts. To account for the compromised electronic structure of gold, promoters are required to improve activity of these catalysts. The ideal promoter must be able to reduce sintering which seems to be the major cause of deactivation [11]. Platinum group metals (PGM) usually have high melting points thus make them ideal promoters. Again they have proved to be the good catalysts over the years in their own systems [12]. There was an economic benefit for using gold over platinum until 2011 when the gold price escalated. Though the prices might have changed there is still a need to replace platinum metal with less costly PGM that have good thermal stability and good catalytic properties. Amongst all the PGM's palladium metal seems to be cheapest compared to platinum and ideal for withstanding harsh conditions, particularly high temperatures [11].

This chapter thoroughly reviews the work reported on gold as a catalyst. These include the structure and the mechanisms displayed by the gold catalysts studied by different research groups. Also the use of bimetallic system is briefly discussed which explains the importance of promoters. The objectives of this study are outlined at the end of this chapter.

## 1.2 Intrinsic properties of gold nano-particle

### 1.2.1 Crystal structure and morphology

Although Haruta's findings were exciting, it perplexed the research community since not much was understood about these catalysts. This posed an obvious challenge to scientists, that is, to study different properties of these noble materials. Even though much time and effort was dedicated in studying the properties of gold nano particles, there is still a lot of disagreement in the literature. As far as the structure and external form of gold nano particles is concerned there is much debate and confusion [13].

Despite the obvious challenge of characterizing such small particles, it is on the other hand extremely challenging to study metal clusters as they are the intermediate between isolated atoms and molecules [14]. One of the other reasons being their reduced atomic coordination resulting in high magnetic moments. After considerable efforts it was discovered that gold nanoparticles have diverse structures [14]. The predicted diverse structures were said to be non crystallographic and multiply twinned particles (MTPs) types [14]. As it is evident that it is challenging to physically characterise tiny particles especially gold particles that have low melting points, conflicting claims have been made regarding the most stable structures of gold nanoparticles [14]. The most stable nanostructures are said to be truncated octahedron, icosahedron, Marks decahedron and cuboctahedron [13, 15] (Fig.1.1).

The five-fold symmetry in icosahedral and decahedral clusters seems to introduce certain stabilising constraints [13]. The icosahedral structure compromises the surface area and packing density. The inward facets in Marks decahedron structure compromise surface area and strain energy [13]. Perfect icosahedral structures are only formed for certain specific number of atoms that is 13, 55, 147, 309, 561, 923 etc [16]. Truncated octahedral shaped particles are usually observed for $Au_{38}$ and Marks decahedron for 75, 77,101 and 146 atoms [16-17]. However, the $Au_{38}$ for truncated octahedron will be predicted to be amorphous by the more metallic n-body potentials. According to the theoretical studies performed by Cleveland et al. the most stable structures are truncated octahedra and Marks decahedra [16]. Perfect cuboctahedral clusters with face centred cubic (fcc) packing can be assembled from the same series of magic numbers as for the icosahedra, and there are other perfect fcc clusters with octahedral or truncated octahedral crystal forms but different special numbers [16].

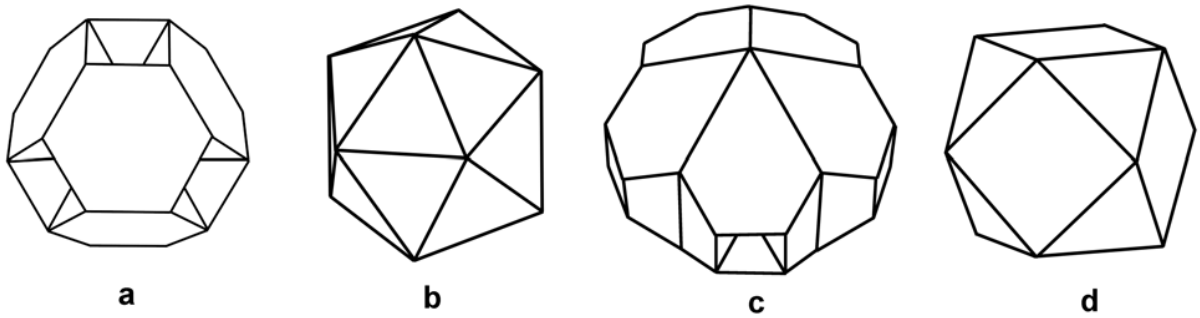



Figure 1.1. Comparison of (a) truncated octahedron, (b) icosahedron, (c) Marks decahedron and (d) cuboctahedron. Note the re-entrant facets in the truncated octahedron and the Marks decahedron. (a) and (c) redrawn from Doye [49], b and d redrawn from Mackay [16].

The fcc-based clusters are generally attained by a combination of crystal facets of the (111) and (100) surfaces whereas icosahedral are comprised of loosely packed (111) surfaces [10, 18-21]. Consequently there will be a difference in surface properties of these structures. This also introduces surface defects such as twins and stacking faults [10, 18-21]. It is difficult to study the structure of a free gold cluster because such clusters are highly unstable in air. Whetten and co-workers have done significant research based on gold clusters passivated by alkythiolates [22-23]. Normally passivated gold clusters by alkythiolates were studied on Marks decahedron and truncated octahedron, while icosahedrons were passivated by citrate sols [13, 19, 24]. It is believed that the passivating surface layer does not perturb the structure significantly hence there will be no substrate interaction observed [19]. Therefore the structure observed will reveal that of a free cluster [19].

It has been claimed that the icosadedron of nominal $Au_{13}$ stochiometry are the particles responsible for catalytic activity in Au/MgO while the hemispeherical fcc cuboctahedral are the active particles in $Au/TiO_2$ [10, 25]. The deactivation of Au/MgO catalyst is due to structural change when icosahedral particles are transformed into the truncated octahedra. This raises questions about the significance and the effect of passivating layer, or could it be that there is discrepancy between the calculations and the experiments [10, 25].

Theoretically $Au_{13}$ is known to be the smallest member of icosahedral clusters [26]. It has the average coordination number of 51 which implies a very low degree of symmetry. Evidently these molecular structures are closely packed with 70% packing efficiency for spherical clusters [27]. Fig.1.2 illustrates the approximate diameters of spherical and hemispherical clusters of different numbers of atoms. The $Au_{38}$ and $Au_{75}$ clusters (Fig.1.2) have a very small diameter of about 1.0 nm and 1.4 nm respectively. The 5 nm clusters that are said to be catalytic active correspond to about $Au_{3600}$ if spherical and $Au_{1800}$ if hemispherical. The most active gold clusters (3 nm) will have about 400 atoms particularly when they are hemispherical.

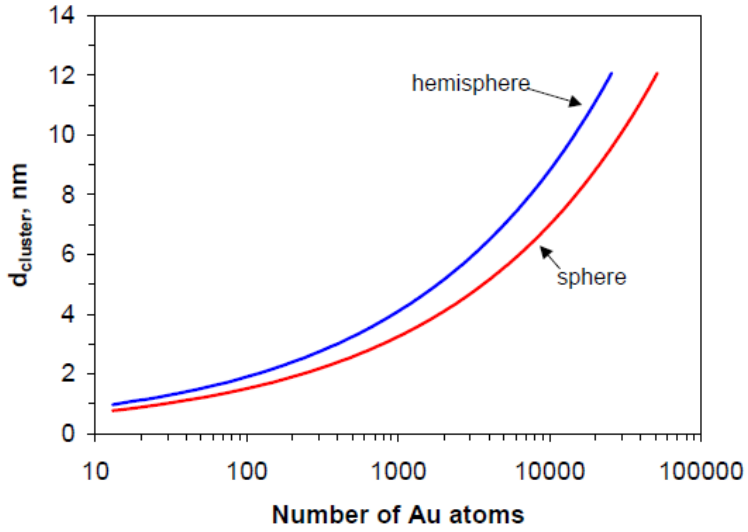



Figure 1.2. Approximate size of nominally spherical and hemispherical clusters of $Au_n$ [25].

However, there is another important aspect that plays a vital role: the substrate. The presence of the substrate will bring about the structural change which will influence the activity of the particles. For example, it has been shown that 2 nm diameter clusters consisting of two layers of about 50 Au atoms each, are active for CO oxidation [28]. Clearly such a structure is too thin to have fcc or hexagonal close-packed (hcp) structure [28]. Given that reproducibility of gold nano particles is often hard to achieve with non-uniform particle size distribution, it is not clear how many particles are responsible for catalytic activity.

### 1.2.2 Electronic structure

The electronic structure of metallic bulk gold may be given as $[Xe]4f^{14}5d^{10}6s^1$ although the $6s^1$ is not readily ionisable in the bulk state, hence explaining bulk gold's inert nature [33]. The electronic configuration of small nano particles is determined from their physical dimensions which are smaller than the characteristic dimension of the electron wave function of the bulk material [27]. Recent studies have shown that reduced gold loses its metallic nature which is chemical dependent especially for particles between 1 and 3 nm corresponding to hemispherical clusters with 14 and 140 atoms [17, 28]. Although it is important to know and understand the electronic structures of both spherical and hemispherical clusters it is somewhat difficult due to the fact that their physical dimensions are smaller than the characteristic dimension of the

electron wave function of the bulk material. Only the electron configuration of spherical clusters was successfully determined [17].

The electronic configuration of spherical gold clusters was determined using a simplified shell model [17]. According to this model all the valence electrons of the atoms of a cluster are placed into a spherically symmetrical energy well, and allowed to distribute themselves. So each individual gold atom will have one valence electron. For example, a cluster of $Au_{19}$ will have an electronic configuration of $(1s^2 1p^6 1d^{10})2s^1$. Hence the $Au_{19}$ will be more reactive than $Au_{18}$ which has $(1s^2 1p^6 1d^{10})$ configuration with filled shells. The notation expresses the accumulation of the entire delocalised valence electrons not those of the individual sub-valence electrons [34-35].

Although the shell model might be beneficial in terms of predicting the electron configuration it has shortcomings that make it questionable. Firstly it could be that the model does not realistically describe the cluster, as it could have acquired only a fractional electronic charge [36-36]. For an example the $½e^-$ charge could be present due to overlap between the electron distribution of an oxide support and the cluster [27]. This may perhaps explain why the two layer clusters of 3 nm are said to be highly active when compared to 0.5 nm particles which deactivate, and yet catalytic activity of gold nanoparticles is size dependent [27-28]. The activity of these particles is associated with the band gap that clearly cannot be predicted by this model [27]. It is said that the band gap of particles below 2 nm increases while the activity is reduced [28]. This strongly suggests the importance of the support, as it brings special transitional electronic structure associated with particular characteristics of the semi-conductors [17, 28]. The same is true for noble metals such as Pt and Pd as they also show similar results [17, 28]. It seems the model also fails to predict the electronic configuration of structures which are less symmetrical and metallic [27]. Nevertheless, the model might have been a great help in terms of explaining the melting point of the gold clusters [27].

Recently, Okazaki et al. studied the electronic structures of supported gold nanoparticles on titania using electron holography method and scanning tunnelling miscrosopy (STM) [37]. Electron holography was used to measure the change in mean inner potential that reflects the distribution of the valence electron density of gold particles. STM was utilized to measure the

local barrier height (LBH) and energy gap. The LBH was useful for estimating the electronic structure and electron distribution of particles. According to these studies the mean inner potential increases when gold supported on $TiO_2$ is below 5 nm. Furthermore, it increases rapidly below 2 nm. The increase in mean inner potential can be related with the size dependence of the catalytic activity of gold nanoparticles [28]. Valden et al. reported that the activity of Au particles supported on the $TiO_2$ (110) surface of the single crystal decreases as the size becomes smaller than 1 nm [37-38]. Recently, it has been that reported that Au two atom layers thick are the most active for CO oxidation [39]. This phenomenon could be explained by the LBH and energy gap measurements. According to these studies the double layer corresponds to a critical height of 0.4 nm, where the Δ LBH of the Au particles supported on the $TiO_2$ (110) surface decreases from +0.3 to 0.0 eV and the energy gap of the Au particles appears. The decrease in energy gap shows that there is a metal to nonmetal transition which is caused by the reduction in the coordination number of the Au atoms as the particle size becomes smaller [37]. This transition is said to be the cause of deactivation of the Au particles supported on $TiO_2$ [37]. Although it is still not known whether there is a positive or negative charge transfer between the gold nanoparticles and the defect site (adsorption surface) of the support it is imperative to understand their catalytic mechanism [27].

### 1.2.3 Melting Point

The melting point of gold nanoparticles is expected to deviate vastly from that of bulk gold due to increased numbers of surface atoms and their electronic structures [19, 29-31]. According to the experimental and theoretical results it is predicted that the melting point decreases with a decrease in particle size (Fig.1.3).

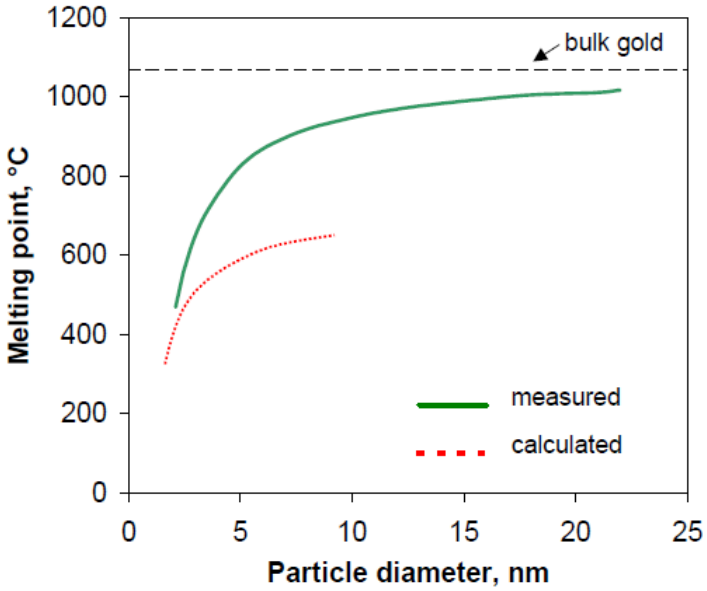



Figure 1.3. Reduction of melting point with a decrease in size of gold nano-particles, showing both theoretical data computed using molecular dynamics [10] and measured data derived from gold nanoparticles encapsulated in silica [38].

Although the experimental and theoretical results shown in Fig. 1.3 may differ, when taken conservatively it is clear that clusters with the smallest size melt at relatively low temperature. The most catalytic active particles of 5 nm (~$Au_{3600}$) would be molten at about 830 °C, particles of about 2 nm (about $Au_{200}$) would liquefy at 350 °C and, by extrapolation, particles of about 1 nm (~$Au_{30}$) at 200 °C [18]. Since it has been reported in the literature that particles in the range of 2 to 5 nm were observed to be active at about 500 °C. This demonstrates the complexity of modelling such a system and shows the need for further studies. However, Dick et al. determined the melting point of silica encapsulated gold particles and confirmed the above results (Fig. 1.3) [30]. According to Dick et al. the same results should be observed for 1 nm supported gold nanoparticles [30].

The other important aspect to be considered is the melting process of different nano gold isomers. Liu et al. showed that morphological difference also plays a vital role in affecting melting point. Liu et al. determined that the melting process involved 3 stages which significantly affects the changes in melting points of clusters irrespective the number of atoms [19]. The three stages identified are: the surface ordering and disordering, followed by surface melting and finally rapid overall melting [19]. During this period there is also structural

evolution taking place. It is said that the melting process usually persists as the molten atoms in the surface can recover the ordering state due to nucleation effect of the matrix still in an ordered state. Finally when all the vertices and edges are disordered, surface melting will resume then structure will become liquid- like resulting in a rounded cluster [19]. Usually at this point the catalysts begin to deactivate [19].

Icosahedra are said to have the lowest melting point whereas Marks decahedra have the highest melting points [19, 32]. However, clusters of different size will have different melting points. At 410 to 420 K there is a structural transition from cuboctahedron to icosahedrons which only occurs for structures with less than 561 atoms. This kind of transition is called quasimelting and usually takes place at room temperature [14]. Once the transition is complete, the icosahedrons will start melting at about 1000 K followed by surface melting. In particles with more than 12,000 atoms, all the isomers show similar melting behaviour except for icosahedral. It is also observed that the melting point increases gradually with the increasing number of atoms [19].

## 1.3 Mechanism of Catalysis

Despite all the experimental and theoretical efforts to understand in detail the behaviour of gold nanoparticles, there is still no agreement in the literature concerning the mechanism of catalysis. Although literature claims that CO oxidation is the most studied and simplest reaction for gold catalysis, its mechanism is still completely not understood [27]. According to literature, few mechanisms have been proposed for CO oxidation. One proposed model is the perimeter model where the active sites for the CO oxidation are on the gold nanoparticles and the defect sites of oxide support together. The second model is dependent on the presence of neutral gold atoms on the gold nanoparticles. This model can further be divided into the geometric and electronic model. The geometric model is based on gold particles that have a high degree of under-coordinated atoms and also a special bonding geometry to other gold atoms that exhibits a more reactive orbital [39, 43-46]. The electronic model is related to the quantum size effect which alters the electronic band structure of gold nanoparticles [47]. It is still not understood whether the charge transfer between the gold nanoparticles and defect sites is positive or negative. According to some researchers the active sites constitute of metallic Au

and $Au^-$ and OH species [48-49]. However, the hemispherical particles are said to show high catalytic activity compared to spherical particles due to the strong metal/support contact [50,51]. Also the type of support has been shown to play a vital role in catalytic activity of gold nanoparticles. Supports are divided into two categories: the active supports which are the reducible and the inert which are non-reducible. The examples of the reducible supports are $Fe_2O_3$, $TiO_2$ and $Co_2O_3$ and the non-reducible are $SiO_2$, $Al_2O_3$ and MgO [54].

The activity of gold nanoparticles is also said to be dependent on different adsorption sites of the substrate as the particle-support interaction varies according to different adsorption sites. Okazaki et al. showed that rutile $TiO_2$ (110) surface has three possible types of adsorption sites (Fig.2.4) which is stoichiometric surface, the surface formed by removing the $O^B$ atoms (Ti-rich surface), and the surface formed by removing the $O^B$ and six-fold titanium ($Ti^6$) atoms (O-rich surface) [37].

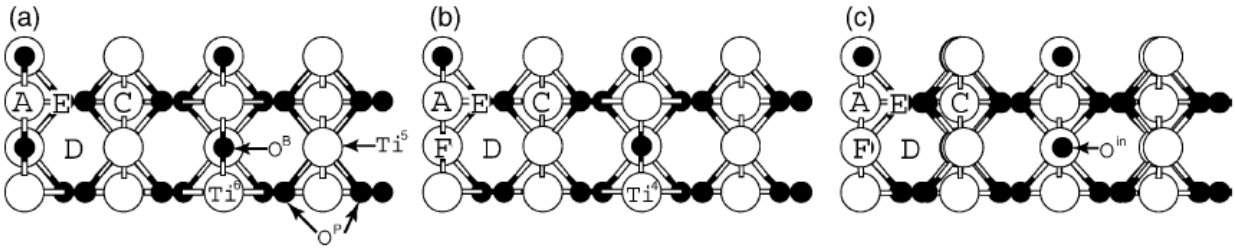



Figure 1.4. Schematic geometry (top view) of $TiO_2$ (110) surfaces. Five possible adsorption sites are marked from A to E for the stoichiometric surface (a) and six possible adsorption sites are marked from A to F for the Ti-rich (b) and O-rich (c) surfaces. The small filled circles and the large open circles indicate the oxygen and titanium atoms, respectively [38].

For stoichiometric surface, atoms adsorb stable in on the on-top site above the five-fold titanium ($Ti^5$) atom or the hollow site surrounded by two $O^B$ and one $O^{in}$ atoms. However, the adsorption energy is quite small and the electron charge transfer and orbital hybridization between gold atoms and the surface atoms is negligible thus stoichiometric sites are not formed in a real $Au/TiO_2$ catalyst. For the Ti-rich and O-rich surface, atoms adsorb more readily on $O^B$ vacant site than $Ti^6$ vacant site. The electron transfer of the Ti-rich surface is from four-fold titanium ($Ti^4$) atoms to the Au adatoms and has higher adsorption energy than stoichiometric surface. The Ti-rich surfaces are usually formed UHV condition. The electron transfer of the O-rich surface is from the Au adlayer to the $O^P$ and $O^{in}$ atoms and has larger adsorption energy

than both stoichiometric and Ti-rich surfaces. According to Okazaki et al. the electron transfer of the O-rich surface seems to comply with the results the holography results where the electron transfer from the Au particle to the $TiO_2$ surface seems to result in an increase in the mean inner potential of the Au particle [37, 40]. He also claimed that the O-rich surfaces should certainly be formed in specimens prepared by deposition precipitation method [37, 41]. However, it was observed that the mean inner potential of samples prepared by deposition precipitation method began to increase at the height of about 5 nm, while that of the sample prepared by vacuum evaporation begins to increase at the height of about 2 nm. Therefore mean inner potential should be dependent on the sample preparation method [37, 41]. According to literature the difference could be due to the different stoichiometry of the $Au/TiO_2$ interface by the two preparation methods. Although the size dependent factor seems to play an important role, Lopez et al. claimed that the key factor is related to the catalytic activity of these particles is the availability of the low coordinated gold atoms on the small particles [42].

### 1.3.1 The active perimeter model

The perimeter model is generally the most accepted mechanism in the literature. According to pioneering work by Haruta, the catalytic activity of metallic gold particles with mean diameter less than 5 nm is attributed by hemispherical gold particles attached on the reducible oxide support. From this work it was generally concluded that the edge of the Au/support interface plays a key role in the mechanism of CO oxidation [53-57]. Fig.2.5 shows a schematic representation of CO oxidation pathways for $TiO_2$ supported Au catalysts. Gold surfaces can adsorb CO when the diameter of Au particles is smaller than 10 nm due to an increase in step, edge, and corner sites [58].

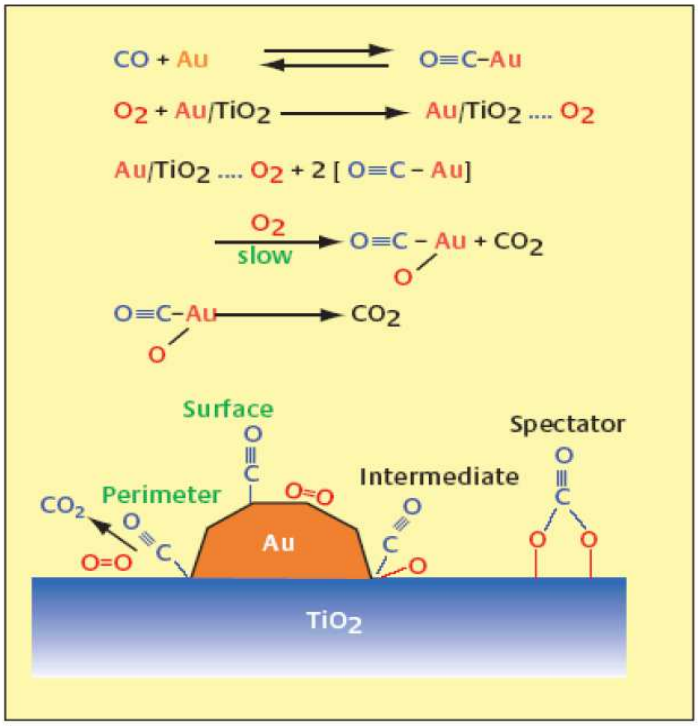



Figure 1.5 CO oxidation reaction pathways of the Au on $TiO_2$ catalyst suggested by Haruta et al. [2-3]

According to this mechanism $O_2$ is chemisorbed at the perimeter interface of Au and $TiO_2$ while CO is adsorbed on the gold surface. The adsorption of $O_2$ is facilitated by the special state controlled by electronic interactions with the oxide substrate. The strong contact of nanoparticles with the support favours $O_2$ adsorption at the perimeter interface. The adsorbed reactants then meet the pheriphery where the reaction takes place. Although the importance of metal support interaction cannot be ruled out the emphasis should also be on the chemical identity of the support [59-60]. Conversely, Grisel et al. have shown how the addition of a little MnOx to an $Au/Al_2O_3$ system was able to stimulate a significant improvement in CO oxidation, by varying the properties of the perimeter without altering the Au particle size or characteristics [61].

Even though this might be the generally accepted mechanism, the adsorption sites of $O_2$ are still not known. The question is whether the $O_2$ is adsorbed on the perimeter itself or the nearby oxide support. Hammer et al. and others showed that molecularly chemisorbed oxygen at the $Au/TiO_2$ and Au/MgO oxide surface and/or interface will readily react with CO to form $CO_2$ [64-65]. Whereas Grisel, Bond and Behm found out that transition metal oxide collects and

dissociates $O_2$ at surface anion vacancies or 'F centres' [48, 66-67]. Behm et al. proposed that the ability of the oxide support to activate oxygen by a superoxo intermediate is essential for the catalytic activity of oxide supported Au [67]. Calculations by Sanchez et al. for $Au_8$ on MgO showed that the $O_2$ should absorb as $O_2^-$ onto gold atoms along the interface perimeter [39]. Although the $O_2$ is adsorbed onto the oxide support, the perimeter surface is equally important.

The other key factor in the perimeter model is the importance of the positively charged Au. Bond and Thompson proposed that the role played by the intermediate layer of $Au^{x+}$ atoms is to attach gold nanoparticles on the oxide support and the oxidized state of these atoms is crucial for the catalytic ability [46]. According to Bond and Thompson's hypothesis Au (III) species stabilize the Au nanoparticles on oxide supports hence Au (III) acts as "chemical glue", between metallic Au and metal oxide supports. According to the proposed mechanism (Fig 2.6) by Bond and Thompson, carbon monoxide molecule is adsorbed on the surface of low coordinated gold atoms. This is therefore attacked by hydroxyl group from either support cation or pheripheral Au (III) ion resulting into the formation of carboxylate group. At this point the oxygen molecule occupying anion vacancy as $O_2^-$ will oxidize the carboxylate group, forming carbon monoxide. The resulting hydroperoxide ion $HO_2^-$ will further oxidizes the carboxylate species forming another carbon dioxide and restoring two hydroxyl ions to the support surface. This completes the catalytic cycle.




$$Au^0 + CO \rightarrow Au^0...CO \quad (1)$$
$$Au^{III} + OH_s^- \rightarrow Au^{II}...OH \quad (2)$$
$$Au^0...CO + Au^{II}...OH \rightarrow Au^{II}...COOH + Au^0 \quad (3)$$
$$O_2 + \square_s^- \rightarrow O_2^-...\square_s \quad (4)$$
$$Au^{II}...COOH + O_2^-...\square_s \rightarrow Au^{II} + CO_2 + HO_2^-...\square_s \quad (5)$$
$$Au^{II}...COOH + HO_2^-...\square_s \rightarrow Au^{II} + CO_2 + 2\,OH_s^- + \square_s \quad (6)$$
$$Au^{II} + \square_s \rightarrow Au^{III} + \square_s^- \quad (7)$$

Figure 1.6 A representation of the oxidation of carbon monoxide at the periphery of an active gold particle on metal oxide support [48]

Supporting evidence from Mössbauer studies showed that the most active catalysts in metal hydroxide-supported systems have the highest fraction of $Au^+$, while EXAFS analysis of Au/γ-$Al_2O_3$ prepared by depositing $AuCl_3$ onto γ-$Al_2O_3$ indicated that activity for CO oxidation requires a polymeric $Au(OH)_3$ precipitate [25,68-69]. The above results were also confirmed by Haruta's group after finding out that $Au^+$ played no role in the activity of Au/$TiO_2$ [49]. The highest activity was observed when all $Au^{x+}$ had been reduced to $Au^0$ by calcination [26]. According to this model the $Au^0$, $Au^{x+}$, and the metal oxide support play a vital role in catalytic activity of gold nanoparticles.

### 1.3.2 The geometric model

For the geometric model the surface of the material is considered important particularly for catalysing the reaction. The dependence of catalyst activity on electronic structure and diameter of particles does not hold. Therefore it is possible for gold clusters of equal size and similar electronic configuration to show very different chemical reactivity [70]. Freund and other co-

workers proposed that catalytic activity of Au nanoparticles for this model is associated with the presence of non-coordinated atoms on the surface of the material. They suggested that if some specific sites such as kinks or defects on the surface of the material, have a particular ability to catalyse a chemical reaction, then the number of these non-coordinated atoms which are not introduced from quantum size effects as a result of particle thickness, are important for optimizing the activity of the catalyst [42, 71-75]. Then the role of the support is to only pin the catalytic particles and prevent them from sintering, hence the chemical identity of the support is less important. The work of Kung et al. supported this by showing that the actual activity of the gold was due to an exceedingly small proportion of the surface gold atoms, about one in a thousand, implying that the reaction occurs at few special sites only [78]. As such an increased surface area of these special sites will result in increased activity. The special sites responsible for catalytic activity are usually found at the edges or other defects and they are considered more electropositive and therefore readily can be ionized to $Au^{x+}$ [46, 76].

Other theoretical investigations suggest that the roughness of Au is vital as it aids in controlling oxygen binding. It is said that the roughness of Au is capable of localizing the highest occupied molecular orbital (HOMO) of Au which in fact is another way of providing a higher electron density at the site where $O_2$ binds. Nørskov and other workers performed further studies on the adsorption strength of CO and found out that it is highly sensitive to coordination site (kinks and steps) and the number of gold atoms [63, 77-78]. These results suggested that the number of low coordinated atoms and corner sites are more important for making Au cluster more active than extended Au surface. Fig. 2.7 shows the dependence of adsorption energies as a function of the Au coordination number. The electronic structure of Au atoms with low coordination numbers has higher lying d states, which interact strongly with the adsorbate states. Recently experimental results has shown that for $TiO_2$ supported Au and unsupported Au catalysts, which are nonporous and has spongelike morphology, do have low coordinated atoms on the metallic gold surface and plays vital role in the mechanism of CO oxidation [48].

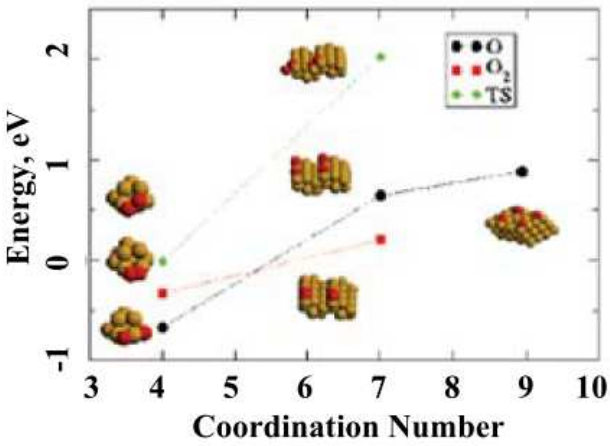



Figure 1.7 Binding energy of different oxygen species, versus gas-phase $O_2$, plotted with respect to the coordination number of the Au atoms of the site. Yellow spheres (Au), red (O), and gray (C) [54]

### 1.3.3 Active electronic model

Although the catalytic activity may occur on the surface of a cluster for this model, the electronic configuration of Au clusters plays a vital role. The purpose of the support material is to modulate the electronic structure. However, it not clear whether both $O_2$ and CO are co-adsorbed onto the catalyst system. It has been shown that catalytically active gold results if Au clusters are deposited onto F-centre (oxygen-vacancy) sites on MgO but not if the F-centres were absent [28, 36]. It is interesting to see that this can either be interpreted as an active-particle or active perimeter hypotheses. If the active-particle model is accepted, then the excess electron density at the F-centre site should be transferred to the cluster and onward to the adsorbed $O_2$ to form the superoxide in order for the catalytic reaction to occur. Indirect evidence was obtained from Valden et al.'s work where it was shown that the catalytic activity of the gold was reduced or absent if it was located on a stoichiometric (i.e. fully oxidised) surface of $TiO_2$ [28]. One would say that such a fully oxidized surface will have very few F-centres and therefore that the gold clusters on it would not be negatively charged and hence not be able to react with $O_2$ to form superoxide. However, for the active-particle model the important part is that the supply of adsorbed $O_2$ which is the rate limiting step, and the reaction can be considerably expedited if $O_2$ can be supplied from the substrate rather than on the nano-particle itself [67]. Based on the above hypothesis, negatively-charged gold clusters $(Au)^-$ play

an important role for the CO oxidation reaction. Therefore, the chemical identity of the support becomes important as different supports can provide different negative charge states [79]. According to literature reducible oxides supports can transfer more charge to Au and Au deposited on these oxides interacts more strongly with oxygen. The metal support interaction provides an ideal environment for $O_2$ activation and the oxidation reaction. Although catalytic activity can vary depending on the supports, Rousset et al. emphasises that key point for the high catalytic activity is not the negatively charged Au but metallic Au [61].

Many studies suggest that the anionic nature Au particles are very important for catalytic activity. On the one hand the cationic $Au^{x+}$ still part take in the catalytic activity of gold nanoparticles thus becoming active species. Previously Bond and Thompson and others proposed on the perimeter model, that Au particles are oxidized into $Au^{+}$ or $Au^{3+}$ sites at the particle support interface and these sites are responsible for the catalytic activity of Au nanoparticles in oxidation reaction [46, 49, 57, 63, 80]. Guzman et al. further suggested that the change in catalytic activity was due to the change in the oxidation state of gold [81]. Furthermore, Hammer et al confirmed the importance of cationic Au after identifying $Au^{+}$-O adhesion bonds of a mixed covalent and ionic nature under more real gold-support interactions and reaction conditions. The importance of positively charged Au species in various reactions like the catalytic hydrogenation of ethane water-gas shift reaction has been reported by Gates et al. and Fu et al. respectively [83].

## 1.4 Factors affecting catalytic activity

Heterogeneous catalytic reactions occur in systems in which two or more phases are present, for instance, solids and liquids, or gases and solids. However, it is particularly important to know and understand the properties of the catalyst. Knowing the properties of the catalyst often gives an idea on how a catalyst can be enhanced in order to obtain optimized catalytic activity. It has become abundantly evident that gold only becomes catalytically active under certain controlled environments, such as low temperature environment [28].

The rapid deactivation of gold-based catalysts for CO oxidation has been reported in the literature. It is for this reason that care should be taken when preparing the gold catalysts as there are specific requirements to be met. However, multiple synthetic routes on how to synthesize supported nano gold catalysts have been developed. So it is important to choose a suitable preparation method, preparation conditions and pre-treatment conditions as they all play role in attaining the small particle size which is one of the most important parameter for the activity of the catalyst.

Since the achievement of small particle size is not always an easy task. There are many experimental variables that play major role hence the reproducibility of catalytic results is rarely accomplished. The reason for deactivation is the sensitivity of the catalyst surface to the pre-treatment and reaction conditions.

### 1.4.1 Quantum size effects

Quantum size effects are known as an impressive effect of the reduced size which results from confinement of electrons [7]. Depending on the structural arrangement of the Au catalyst on the support, catalytic activity can change [84]. Goodman's group referred to quantum size effects in order to explain a maximum catalytic activity of Au particles in CO oxidation. They proposed that particle thickness may be the key parameter responsible for catalytic activity in the case of two atom layed Au particles [27, 39, 70, 84-85].

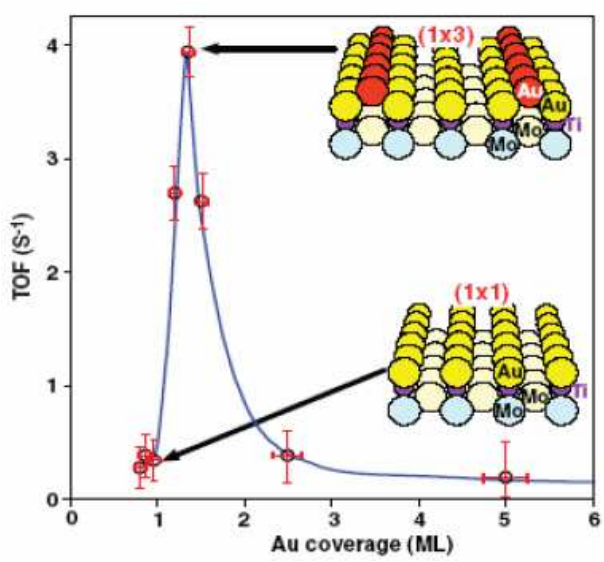



Figure 1.8 Activity for CO oxidation at room temperature as a function of Aucoverage above the monolayer $TiO_x$ on Mo(112) [43]

Au with a partially bilayered structure prepared on a $TiO_x$ film grown on a Mo (112) surface shows an increased activity, more than an order of magnitude higher with respect to monolayered structure (Fig. 2.8). To eliminate the particle shape and direct support effects a completely wet oxide support was used in both monolayered and bilayed systems. Further studies confirmed that the catalytic activity of Au particles was indeed dependent on thickness [69].

The high catalytic activity of the Au bilayer system was explained in terms of the electronic charge of Au, the binding strength of the reactants, and limited dimension effects. This was supported by DFT calculations of Hernadez at al. [86]. It was said for highly active Au catalysts, CO molecule binds directly to the on-top site of Au atom and the molecular oxygen adsorption is energetically unstable. Therefore the adsorbed CO captures an oxygen molecule to form a $CO\text{-}O_2$ intermediate complex (peroxo-type in Fig. 2.9). The formation of peroxo-type complex is in agreement with the experimental and theoretical results [43, 52]. After formation of $CO\text{-}O_2$ intermediate complex, the O-O is dissociation will occur resulting in $CO_2$ and the remaining oxygen atom will bound onto the nearby Au atoms, which will further react with CO [45]. The above result was explained by larger electron density that around the bottom Au layer which favoured a charge transfer into the antibonding $2\pi$ orbital. This charge transfer obviously weakens the O-O bond and consequently leading to the oxygen activation [86-87].

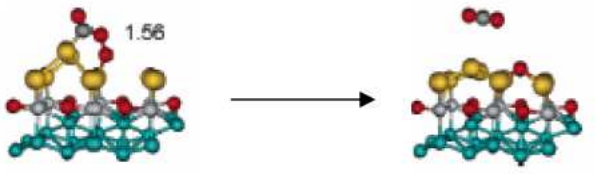



Figure 1.9 Structure of the peroxo-type CO-$O_2$ complex (left) and final state (right) for CO oxidation on the 4/3 layer Au/TiO-Mo(112) surface [86]

## 1.4.2 Cluster size effects

According to studies reported by Valden and Bamwenda et al. the catalytic activity of the Au clusters supported on $TiO_2$ for the CO oxidation reaction was attributed by the size effects with the maximum activity at a range of about 3.5 nm [27, 88]. Lee et al. also agreed that catalytic activity of gold particles is strongly dependent on the deposited cluster size, because electronic and geometric structures are both size-dependent [89]. Fig. 2.10 below shows an $Au_7$ cluster on $TiO_2$ with the highest catalytic activity toward CO oxidation reaction. According to the results of Heiz and co-workers, significant reactivity for clusters as small as $Au_8$ was observed for CO oxidation reaction of Au/MgO system [35].

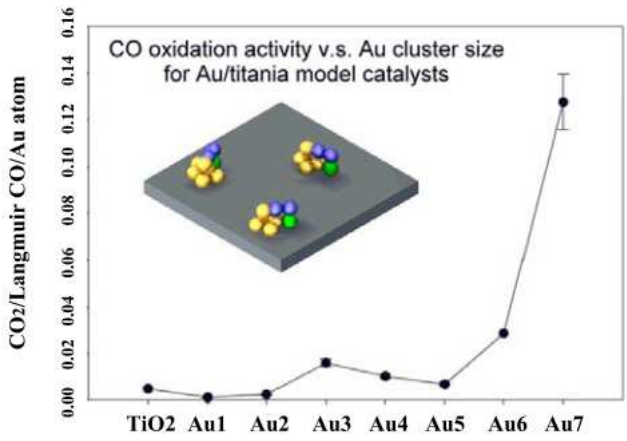



Figure 1.10 Size dependence of CO oxidation activity [90]

Mill et al. claimed that the finite size of small clusters leads to better binding because the HOMO is more localized this is known as confinement effect [91]. The finite size prevents of the cluster prevents the delocalization of the HOMO. This effect said to facilitate the charge transfer into the $\pi^*$ orbital of $O_2$, which induces the molecule to bind to gold.

### 1.4.3 Moistures effects

It has been reported that the presence of moisture enhances the catalytic activity of gold catalysts. Experimental results have shown that the presence of moisture on Au catalyst, increases catalytic activity up two orders of magnitude which is unusual for other common catalysts [91-95]. Date et al. reported that the activity is mainly affected by the amount of moisture adsorbed on the catalysts. However, higher concentration of moisture suppresses catalytic activity as the active sites are blocked [92]. The theoretical work of Landman et al. revealed that coadsorption of $H_2O$ and $O_2$ (Fig. 2.11b) leads to formation of a complex well bound to the gold cluster. And the CO induced proton transfer results in formation of a hydroperoxyl-like group (left) and a hydroxyl (right) in Fig. 2.11c. Consequently the O-O bond is activated, leading to a weakened peroxo or superoxolike state, and the reaction with CO to form $CO_2$ occurs with a small activation barrier.

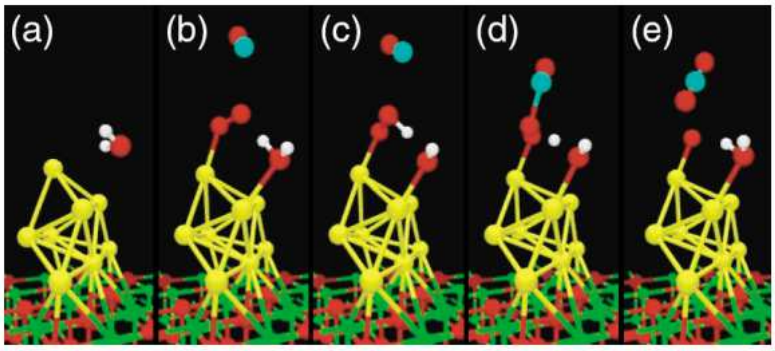



Figure 1.11 Atomic configurations displaying several stages in the simulation of the coadsorption of $H_2O$ and $O_2$ on the top facet of a Au8 cluster supported on MgO(100), and the subsequent reaction with gaseous CO to form $CO_2$ . Yellow (Au), red (O), white (H), green (Mg), and aquamarine (C) [98].

Gold-based catalysts have some unusual and useful features, in particular their high activity at comparatively low temperatures and their tolerance to humidity. Gold's efficacy as a catalyst is believed to be the result of its very low chemical reactivity which ensures that adsorbed reacting species are for the most part only weakly bound [28]. The low reactivity of gold is believed to be inherited from inert bulk properties [28]. The catalytic surfaces are achieved readily only when the gold is exposed as nano-particles or nano-porous surfaces. To explain the

reactivity of these particles actually requires more than one mechanism. This could be because of highly sensitive properties of nano gold particles [28].

### 1.4.4 Support effects

Although there are many other factors known to play role in the catalytic activity of gold particles, the support is said to be for the activity of Au catalysts. The real reason why the support effect is claimed to be the major contributor in activity of gold catalyst, it is due to its ability to stabilize gold nanoparticles, provide active sites at the metal-support boundary, and influence the oxidation state of gold [97]. One of the most important aspects is the choice of support as they are classified as either active or inert supports. The active supports are reducible because they can activate and store oxygen, whereas inert supports may not be able to supply reactive oxygen for CO oxidation [66]. Examples of reducible supports are $Fe_2O_3$, $TiO_2$, $NiO_x$ and $CoO_x$ and examples of inert supports are $Al_2O_3$ and $SiO_2$. Gold on $Fe_2O_3$ has been reported to be active for CO reaction at temperatures as low as 197K (-76°C) [60, 65]. Excellent and sustained activity was obtained when catalytic gold nano-particles are combined with the already catalytic mixed $MnO_x$-$CuO_y$ oxide ('hopcalite') [61, 98]. $SiO_2$ catalyst was shown to have low activity for CO oxidation. The low activity of the $SiO_2$ catalyst was due to negatively charged Au $(OH)_4$ species which are difficult to adsorb onto the negatively charged $SiO_2$ [66].

However, there are specific factors of the support that could account for the high catalytic activity observed particularly for CO oxidation reaction. Literature reveals that there have been studies dedicated into understanding the properties of the typical oxide supports used for gold catalysts. In extensively trying to understand properties studies were done on the synthesis methods and morphology [2, 99–104]. The different modifying agents for oxide supports were also studied [2, 99–104]. Understanding the properties of the support it could give a clear and deeper understanding on the support effects, particularly the surface of the support.

### 1.4.4.1 Effect of the particle size of the support

Numerous studies as reported in the literature have considered gold supported on pristine supports. Pristine supports are $TiO_2$, $CeO_2$, $Fe_2O_3$, $ZrO_2$, $Al2O_3$ and $SiO_2$. The rationale for using pristine support is because they are commercially available, and it is comparatively easy to establish the structure-property correlation if a supported catalyst is composed of only a metal and a pristine support [97]. Another reason is that in the early publications of Haruta and co-workers, they used pristine supports; subsequently researchers have continued to use such supports to load gold [5-6, 49]. It has been established that the Au/support catalysts have simple metal-support interfaces, the size and shape of supported particles may have a more profound influence on the performance of supported gold catalysts.

Despite the common use of commercial oxide supports the effects of particle size and shape of the supports are often not addressed [97]. Rolison and co-workers studied fabricated Au–$TiO_2$ composite aerogels by adding gold colloids (~2 nm) to a $TiO_2$ sol prior gelation [61, 75]. Removing the organic capping agents by calcination increased the particle size of gold nanoparticles to about 6 nm and the crystalline size of anatase was about 10-12 nm when compared that of the gold nanoparticles. The high catalytic activity of this catalyst was obtained particularly for the oxidation of CO. It was suggested that the resulting catalytic activity was due to the strong contact of gold nanoparticles with small sized $TiO_2$ particles, which creates more interfacial active sites [105-106]. As such it was anticipated that the amount of active sites will decrease as the size of the support is larger than that of gold particles. Xu and co-workers further explored the size effect of zirconia in Au/$ZrO_2$ catalysts for CO oxidation [107]. They found that the Au/$ZrO_2$ catalyst with gold particles of about 4–5 nm in diameter and $ZrO_2$ nanoparticles of 5–15 nm were extremely active for the CO oxidation as compared to larger $ZrO_2$ particles of 40–200 nm [107]. From the above mentioned results the authors suggested that the reduction in the particle size of the support may not only create more contact between the metal and support, but it also creates more oxygen vacancies which have the ability to activate oxygen and allow more oxygen migration easily [108]. Shen and co-workers confirmed this by studying several gold catalysts with similar gold particle sizes on $ZrO_2$ supports of various particle sizes, and established that the activity in the water–gas shift reaction decreased when the size of $ZrO_2$ support particles was increased [109]

However, it was not certain whether the gold particle size changed as the size of support was varied. The TEM experiments further confirmed that by varying the particle size of the metal oxide supports the sizes of gold nanoparticles were not drastically changed [110]. In contrast Bokhimi and co-workers reported that the surface area of the $TiO_2$ support decreased with increasing treatment temperature, and the crystallite size of the support increased which increased the size of gold nanoparticles [112]. They also suggested that the resulting low surface area of the support may lead to higher local concentrations of gold species and fewer pinning centers on the support surface, causing particle agglomeration and low catalytic activity for CO oxidation. It was concluded that it is difficult to monitor the effect of particle size of the support when both particle size of the support and the size of gold nanoparticles are varied [97]. Other properties such as morphology of the support could also be explored and maybe have a better effect.

### 1.4.4.2 Effect of the particle morphology of the support

It has frequently been demonstrated that the particle shape or morphology of the support has a profound influence on the catalytic activity of gold catalysts [25]. This is not surprising considering that morphology of gold particles also plays a role in the catalytic activity of these nanocomposites. However, it is intriguing given the fact that Au/support catalysts with differently shaped support particles have gold-support interfaces with similar chemical components [70]. In order to demonstrate the effect of morphology of the support, studies have been employed on the support with exotic morphologies. Han and co-workers studied gold nanoparticles supported on γ-$Al_2O_3$ nanofibers and found it was highly active for CO oxidation as compared to the gold supported on commercial γ-$Al_2O_3$ with irregular shape [70]. They concluded based on the diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) data, that the high activity was facilitated by the hydroxyl group bonding to the γ-$Al_2O_3$ nanofibers. Zhong and co-workers also showed that gold dispersed on porous α-$Fe_2O_3$ nanorods was more reactive for CO oxidation than gold nanoparticles dispersed on commercial α-$Fe_2O_3$ [111]. Wang and coworkers loaded gold on β-$MnO_2$ nanorods and found it was more active than Au/commercial β-$MnO_2$ particulates in the solvent-free aerobic oxidation of alcohol [112]. The authors postulated that the high activity was attributed by the presence of more cationic

gold species and surface oxygen vacancies resulting from the strong interaction between gold and the reactive surface of the $MnO_2$ nanorods [112].

Flytzani-Stephanopoulos and co-workers also studied the activity of gold nanoparticles supported on $CeO_2$ nanorods, nanocubes, and nanopolyhedra [113]. It was found that the activity in the water–gas shift reaction followed the sequence $Au/CeO_2$ nanorods > $Au/CeO_2$ nanopolyhedra>$Au/CeO_2$ nanocubes. They suggested that the low activity of $Au/CeO_2$ nanocubes was caused by the predominant metallic gold species on the support surface and negligible metal–support interaction, as shown by X-ray photoelectron spectroscopy (XPS) and hydrogen-temperature programmed reduction ($H_2$-TPR) [113]. Wang and co-workers synthesized spindle-shaped $Fe_2O_3$ nanoparticles using acidic amino acid additives, and they also prepared rhombohedral $Fe_2O_3$ nanoparticles using basic amino acids [114]. The particle size of the support could be controlled by varying the concentration of the amino acids. Gold nanoparticles were loaded on the support by colloidal precipitation and observed that the spindle shaped $Au/Fe_2O_3$ showed higher activity, even though the sizes of gold nanoparticles on the two supports were comparable 3–4 nm and the particle sizes of the supports were also very similar about 80 and 77 nm, respectively. It was suggested that rough surfaces or edges or defects of the spindle-shaped $Fe_2O_3$ were responsible for high activity.

Although the above mentioned studies has shown that by varying the support morphology results in dramatic increase in catalytic activity, the fundamental reasons for the observed activities are still not clear. As such more studies are still needed to explain the dramatic influence in activities. Besides the different shapes of the support, it cannot be ruled out that different preparation methods and different levels of residual organic or inorganic species on support surfaces do influence the catalytic activity of these catalyst in one way or the other. The same can be said about activity of gold particles supported on different crystal phases of $TiO_2$ (anatase, rutile, brookite) [115]. Although there is a real difference in catalytic activity of gold supported on the different crystal phases of $TiO_2$, it is not yet clear whether the difference is due to the properties of the support, or due to the difference in preparation methods. Although there maybe interplay between size effects, shape effects, crystal phase effects, impurity effects, it is important to consider the effect of other unknown factors such as different synthesis procedures or synthesis details. Therefore it is dangerous to conclude that the difference in catalytic activity

could be due to one single factor. Incorporating other additional components such as modifiers and additives could aid in building a desirable catalysts with enhanced activity.

### 1.4.4.3. Interfacial structure engineering

The achievement of more desirable catalytic architects is established by incorporating additional components which are capable of modifying the structural properties and tune the catalytic properties [116]. There are three strategies adopted to make such heterostructured gold catalysts, depending on the sequence of introducing gold and the modifier or additive. The three strategies of modifying gold catalysts are pre-modification, post-modification and the co-addition strategy [97]. In pre-modification strategy, a catalyst support is first treated by a modifier, and gold is subsequently deposited onto the pre-modified support. For post-modification strategy gold is first loaded on the support and modifier is added. In co-addition strategy, gold and inorganic components are simultaneous added. Adding modifiers construct modifier-support interfaces which result into new active sites and high stabilized gold nanopaticles [97].

#### 1.4.4.3.1 Pre-modification of the support

It is known that $SiO_2$ is not suitable for dispersing gold nanopartles via deposition precipitation method due to the low isoeletric point (IEP ~2) of $SiO_2$. The low IEP of $SiO_2$ does not allow effective absorption of $Au(OH)_4$ species onto the negatively charged $SiO_2$ surface under basic conditions. One way of overcoming this obstacle is to introduce a high isoelectric point metal oxide onto the $SiO_2$ surface. $TiO_2$ support was introduced by surface-sol-gel technique under non-aqueous conditions (Fig. 2.12) [115,117].

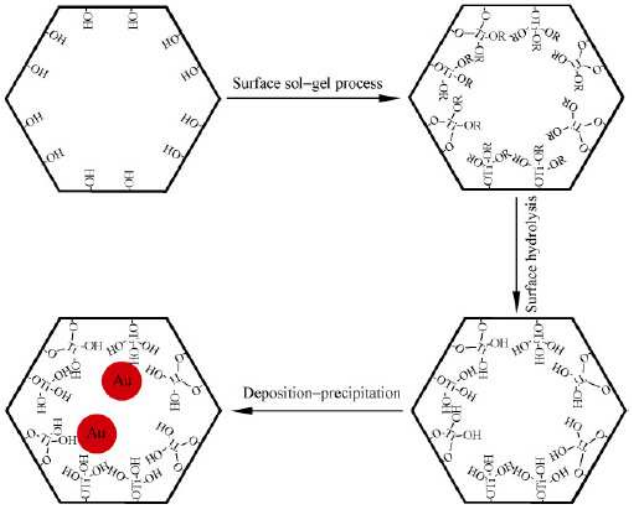



Figure 1.12 The modification of mesoporous $SiO_2$ by $TiO_2$ using a surface–sol–gel approach for loading gold nanoparticles. [116]

In this approach the $TiO_2$ surface is loaded with a Ti $(OC_4H_9)_4$ precursor and methanol and toluene were used as the solvents. The $Au/TiO_2/SiO_2$ catalysts showed high activity for CO oxidation as compared to the $SiO_2$. The enhanced activity was not only attributed to the high gold loading on of $Au/TiO_2/SiO_2$ compared to that of $Au/SiO_2$, but it was also influenced by the presence of an active Au–$TiO_2$ interface [116]. It has been reported in the literature that other pre-modification strategies on the prepared $SiO_2$ based catalysts such as $Au/Al_2O_3/SiO_2$, $Au/TiO_2/SiO_2$, $Au/FeO_x/SiO_2$, $Au/CoO_x/SiO_2$, $Au/ZnO/SiO_2$, $Au/LaO_x/SiO_2$, and $Au/CeO_2/SiO_2$ are also effective. Although promoters were utilized for improved activity, some of the catalysts were not active as anticipated particularly for CO oxidation [104, 117-138, 141-144]. Besides low activity of these catalysts, interfacial characterization were not performed, therefore the reasons for enhanced activity were not clear. As such it was not known whether the modification effect was on the oxidation state of gold, the size of gold nanoparticles, or the creation of new gold–modifier interfaces.

To prevent sintering of $Au/TiO_2$ catalysts at high temperature, amorphous $Al_2O_3$ was used to increase resistance to particle sintering. The $Al_2O_3/TiO_2$ support was synthesized by surface–sol–gel processing of Al $(sec\text{-}OC_4H_9)_3$ on $TiO_2$ followed by controlled hydrolysis [97]. The $Au/Al_2O_3/TiO_2$ underwent minimal thermal deactivation at the same temperature as $Au/TiO_2$ and showed high activity for CO oxidation [43,145]. The authors proposed that addition of

metal oxide may induce different redox properties, which could have an effect on the oxidation states of gold and create new active sites hence enhanced activity. The pre-modification strategy has also been used to prepare catalysts such as $Au/MgO/TiO_2$, $Au/MnO_2/TiO_2$, $Au/FeO_x/TiO_2$, $Au/CuO_x/TiO_2$, $Au/ZnO/TiO_2$, and $Au/CeO_x/TiO_2$ [146-153]. But in most cases the local interfacial structures were often not characterized sufficiently.

However, the development of $Au/M_xO_y/TiO_2$ catalysts proposed another explanation in contrast to what Xie and Tang mentioned about modification of an $Al_2O_3$ support by $La_2O_3$. They had proposed that modification of an $Al_2O_3$ support by $La_2O_3$ could stabilize metallic nickel particles for CO methanation [154]. In contrast Liu and co-workers showed by density functional theory (DFT) calculations that the binding of gold on $Al_2O_3/TiO_2$ was much stronger than that of gold on $TiO_2$ [155]. The DFT calculations were done under the assumption that that $Al_2O_3$ was dispersed homogeneously on $TiO_2$ support. The obtained results showed that the activity of CO oxidation on $Au/Al_2O_3/TiO_2$ was low if $TiO_2$ was fully coated by $Al_2O_3$. Therefore, they concluded that the $TiO_2$ should not be fully coated by $Al_2O_3$, to provide more contact of gold nanoparticles with both the $TiO_2$ support and $Al_2O_3$ patches [155]. Ma and co workers proposed that the coating of $Al_2O_3$ on $TiO_2$ support may not be homogeneous and several $Au/Al_2O_3/TiO_2$ catalysts with a range of $Al_2O_3$contents are all active catalysts. In an attempt to validate this assumption Hagaman and co-workers conducted a solid-state 27 Al magic angle spinning (MAS) and triple quantum magic angle spinning (3QMAS) NMR to investigate different $Al_2O_3$ loadings on $TiO_2$ which were calcined at different temperatures [156]. The authors showed that the highest catalytic activity and the smallest gold particle size reported in the literature correlated with the maximum number of monolayer-type octahedral $Al_2O_3$ species on the $TiO_2$ support. [44]. Although pre-modification of the support do have an effect on the catalytic activities of these catalysts more studies are still need to be conducted so that it can be clearly understood what does the modifier induce on the catalysts.

### 1.4.4.3.2 Post-modification of the supported catalysts

Although $Au/TiO_2$ is known to be active for CO oxidation at ambient temperatures (as low as -76 °C) it also suffers from sintering of the gold nanoparticles at high temperatures (from 200°C)

[97]. The post modification applied on these catalysts to overcome sintering is loading gold nanoparticles on $TiO_2$, and then soaking the $Au/TiO_2$ in an aqueous $H_3PO_4$, followed by extensive washing [78]. The $H_3PO_4$ additive had a strong stabilization effect on the gold nanoparticles and the $H_3PO_4$ $Au/TiO_2$ catalysts were still active for CO oxidation after high-temperature treatment. However, there was no dramatic increase in catalytic activity as the $H_3PO_4$ catalysts showed the same activities for both thermally treat and untreated catalysts. Despite the stability effect that $H_3PO_4$ additive have it also has a detrimental effect as it can cause deactivation of the catalysts [97]. Hutchings and co-workers have demonstrated that the addition of small amounts of $NaNO_3$ (0.00625 and 0.0125 wt% Na) to $Au/TiO_2$ led to significant enhancement in CO oxidation activity, whereas excess $NaNO_3$ (0.0375 wt% Na) deactivated the catalyst [157].

Other post modification strategy used in the literature is the addition of $SiO_2$. The $SiO_2/Au/TiO_2$ catalysts were prepared by a solution-phase chemical grafting of $Si(OCH_3)_4$, $(C_2H_5O)_3Si(CH_2)_3NH_2$, or $((CH3)_3CO)_3SiOH$ onto $Au/TiO_2$ [158]. It was found that the untreated catalysts still containing organic fragments were low in activity whereas the thermally treated catalysts were still active for CO oxidation at 700°C. However, the addition of $SiO_2$ to $TiO_2$ support did not improve activity. So it was concluded that the role of $SiO_2$ is restricted to the mitigation of the sintering of gold nanoparticles at elevated temperatures. Another method of post modifying the $Au/TiO_2$ catalysts was reported in the literature. Amorphous $SiO_2$ was utilized to post modify the $Au/TiO_2$ via gas-phase atomic layer deposition (ALD) method (Fig.2.13). After the thermal treatment at high temperature it was found that the gold nanoparticles were still small in size and there was no significant improvement in catalytic activity.

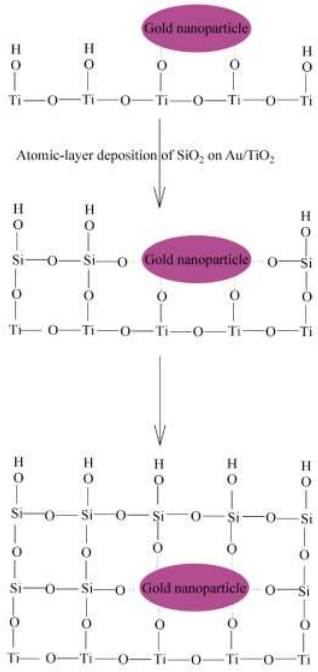



Figure 1.13 Schematic representation of the ALD of amorphous $SiO_2$ onto $Au/TiO_2$ [82]

The difference obtained resulted from different methods used for post modification. The $SiO_2$ matrix formed via solution-phase chemical grafting was assumed to be porous, whereas the $SiO_2$ matrix fabricated via atomic layer deposition was the least porous. Furthermore, similar preparation methods have been used to prepare sintering-resistant catalysts such as $SiO_2$/Pt/MFI zeolite, $SiO_2$/Pt/C, and $SiO_2$/Pt/$Fe_2O_3$ [159-163]. To explain the stabilization effect of $SiO_2$ on $Au/TiO_2$ catalysts, Rashkeev and co-workers conducted a first-principles DFT study, and established that the deposition of $SiO_2$ on a $TiO_2$ support may cause lattice-mismatch instabilities and lead to the construction of strong anchoring sites for gold nanoparticles, even when the coverage of $SiO_2$ is below monolayer [164].

The above mentioned examples are some of the ways in which support modification can be done. However, there are many ways in which the support can be modified in order to improve catalytic activity of supported gold catalysts. Even exotic supports can also be modified by implementing some of the above mention methods of modification. Again, modification strategies can be employed to form bimetallic systems of supported gold catalysts.

Catalytic activity of gold catalysts can be improved by improving the diversity of the morphology in order to attain more complex metal-support interfaces, enhancing the thermal stability of gold catalysts, and adding more functionality to the catalyst system. As such the development of gold catalysts has yielded diverse opportunities for further fundamental and applied research [165–171]. Even though many viable ways have been developed to improve activity of gold catalysts particularly at high temperatures they still suffer from rapid deactivation. In some cases the additives intended to enhance activity and/or the selectivity of the catalyst may act as an inhibitor resulting in deactivating the catalysts.

## 1.4 Deactivation of gold catalysts

Catalyst deactivation is one of the main problems to circumvent for practical catalysis. It is caused by changes in morphology and chemical composition of the surface or bulk catalyst which is assumed to take place during the reaction. Therefore it is anticipated that gold catalyst will also suffer similar effects considering their sensitive nature. It is common knowledge that sulphur and phosphorus are among the few elements with a strong affinity for metallic gold [25]. Therefore, it is anticipated that gold catalysts will readily deactivate in the presence of these metals, particularly if they are in non-oxidised forms [25]. According to the study on the effect of $SO_2$ it was found that $Au/TiO_2$ is rapidly poisoned [172]. Furthermore, it was claimed that Au-containing catalysts are far more resistant to deactivation in liquid phase reactions than their PGM counter-parts [173], implying that they may be more resistant to poisoning in some instances. Again halogens are also known to have a strong affinity for gold catalyst, chloride being the most commonly known [75,174]. In the case of chlorine the poisoning is likely to occur during the manufacturing of the catalyst, for example, when $HAuCl_4$ is used as a starting material.

Deactivation of gold catalysts could also be due to combinations of sintering and Oswald ripening which causes increased particle size and a reduced specific surface area [25]. However, there are three factors that can exacerbate the problem. Firstly, the melting point of gold nanoparticles which is reduced compared to bulk gold, secondly the local heat of reaction will raise the temperature of the nano-particles above that of the catalyst chamber and substrate,

and the third is the chloride, a common residual impurity that appears to facilitate the sintering process [75]. However, it has been reported that sintering is retarded when the gold is supported on rough surfaces [28].

Another cause of deactivation of gold catalyst involves the deposition of carbon or graphite onto their surfaces. This problem was observed for gold-catalysed hydrochlorination of ethyne, particularly at elevated temperature processing hydrocarbons [175]. It has been said that addition of Au to the catalyst system will either have a retarding effect or will eliminate the coke completely [176].

For gold catalyst systems in CO oxidation, deactivation could be the result of phase transitions such as the formation of carbonates and/or blocking the active sites [187]. Oh et al. also demonstrated that thermal treatments of the catalyst in dry He at 100$^{o}$C or higher deactivated the catalyst [189]. Bond and Thompson and other workers proposed that the thermal treatment modify the catalyst by removing the hydroxyl groups from the ionic Au species and from the surface of the support, ultimately resulting into agglomeration [186].

It is also claimed the oxidation state of Au could deactivate the catalyst. For example any gold-based catalysts that require the presence of oxidised Au, such as $Au^{3+}$, can be deactivated by the reduction of it to $Au^{0}$. It was demonstrated that the $Au/Co_2O_3$ and Au/NiO catalyst showed a rapid deactivation at elevated temperatures for WGS reaction [177].

Although it has been shown that gold-based catalysts used for CO oxidation suffer from rapid deactivation, attempts have been made to enhance catalytic activity. In some instance the activity has been improved by either optimizing reproducibility or incorporating catalyst promoter. The use of additives and bimetallic systems has been reported in the literature.

## 1.5 Bimetallic systems

It is anticipated that applying nanotechnology in catalysis will aid in producing a new generation of catalysts by design. It has been said that nanotechnology is an approach needed to

provide precise control of selectivity and activity in catalytic reactions, particularly for gold based catalysts, whose catalytic properties have been claimed to be remarkable [178].

For many systems, bimetallic catalysts have been shown to have synergistic catalytic performance which differ from either their individual counterparts [179-182]. The bimetallic components are said to have a significant effect on the composition and particles size of catalytic particles [183]. The improved properties of bimetallic metal catalysts are generally attributed to either ensemble or ligand effects, although other factors, related to particle size and matrix have been reported [184].

The structures of bimetallic catalysts are usually complicated and multiform [178]. During preparation of bimetallic catalysts there are three possible structures that can be identified, that is, core/shell, heterostructure, or intermetallic and alloyed structures (Fig 1.14). [184-185].

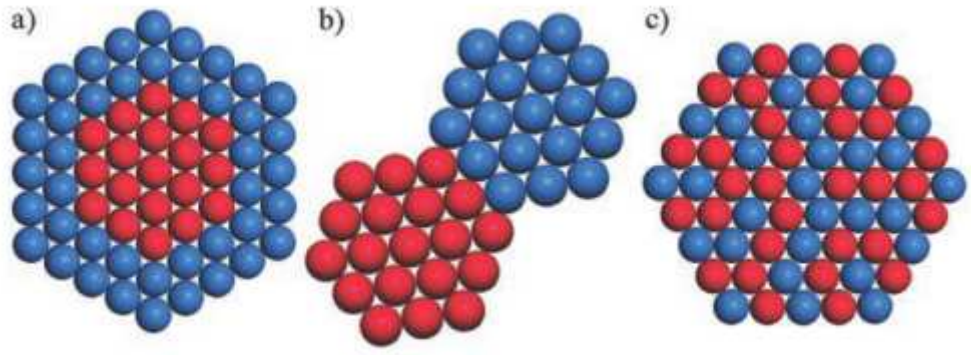



Figure 1.14. Bimetallic Nano Crystals with different structures: a) core/shell; b) heterostructure; c) intermetallic or alloyed structures [178].

For the formation of core/shell structures (Fig 1.14a), one type of metal ions is reduced first and forms an inner core, another type of metal atoms prefers to nucleate and grow surrounding the core to form a shell because separate nucleation is more difficult. Nucleation of two metals may occur under proper conditions leading to a growth of two kinds of metal atoms. If the mixed interface occurs during the growth process, heterostructures (Fig 1.14b) may be formed. The intermetallic and alloyed bimetallic structures vary from the core/shell structures as they are composed of homogeneous mixtures of two metals and metal-metal bonds form. The difference has clearly been shown by the powder x-ray diffraction (XRD), for core/shell or heterostructure

compounds, the characteristic diffraction peaks of two different metals can be distinguished. Whereas, for the intermetallic and alloys the characteristic peaks of individual metals disappear and new Bragg reflections can be observed, indicating formation of new compounds. Although preparation methods for monometallic catalysts have been developed it is still a major challenge to obtain controllable bimetallic catalysts. Difficult synthetic processes are said to be inherited from the complexity and formation of multiphase bimetallic [178].

### 1.5.1 Platinum Group Metals (PGM)

Platinum group metals have been widely explored in catalysis. The PGM's are claimed to be very efficient oxidation and hydrogenation catalysts [189]. Platinum group metals are a group of six metals which behaves the same chemically and are dense. Platinum and Palladium are soft, ductile and resistant to oxidation and high temperature corrosion. They have widespread catalytic uses. In industry they are often utilized with the addition of other metals, including other PGM's. Palladium has been called "the least noble" of the noble metals because it is the most reactive of the platinum group. Therefore, the use of palladium metal could have a stabilization effect on the supported gold nanoparticles, particularly at high temperatures [190]. It has been reported that supported gold catalysts suffers from rapid deactivation at high temperatures which is mostly caused by agglomeration of particles.

The Au/Pd system has been extensively studied as the two metals are miscible in almost all the composition and reactivity of palladium and gold has been reported for liquid phase oxidation with oxygen [191-195]. It has been claimed that these catalysts were highly active and resistant to poisoning [195]. The synergistic effect between gold and palladium metals is a well-recognized phenomenon in heterogenous catalysis [196-201]. However, formation of multiple phases has been reported, thus making it difficult to identify reactive species [202]. For catalytic purposes, highly dispersed small, nano- particles are important including the thermal treatment [202]. Enache et al. have recently shown that Au-Pd catalysts supported on $TiO_2$ gives high turnover frequencies for oxidation of alcohols [203]. Recently Chen et al. have reported high activity of Au-Pd catalysts for VA formation [38]. The high activity of the Au-Pd catalysts was explained by the presence of Pd atoms on the surface [38]. A bimetallic core shell

structure, consisting of a Au-core with a Pd-shell was shown to increase the activity of Pd nanoparticles for the hydrodechlorination of trichloroethylene by a factor of 15 [204]. After optimization of the particle size (4 nm) and degree of Pd coverage (highest activity with 12.7 wt % Pd) of the Au-nanoparticles, an increase in activity by a factor 34 was observed [205]. De Corte et al. reported high activity for the bio-Au-Pd and bio-Pd/Au catalysts [190]. The Pd/Au bio catalysts showed a change in the lattice structure indicating formation of unique bimetallic Au and Pd structure. A lattice contraction of bimetallic crystals compared to monometallic particles has been demonstrated for crystals of Pt/Cu and Pd/Co. [206-207]. It was suggested that the promotional effect was likely due to a beneficial geometric effect of Au on the positioning of Pd within the crystal. The presence of Au causes a contraction of the lattice resulting in a structure which can enable the contact between the two reacting substances [190].

## 1.6 Motivation

The increasing levels of hazardous substance in the atmosphere have become a great global concern. It has been recognized that the current climate change represents an urgent and potentially irreversible threat to human society and the planet, and thus hence it draws a great concern. The United Nations Framework Convention on Climate Change (UNFCCC) is an organization formed to combat global warming. This organization started the Kyoto protocol which was adopted on 11$^{th}$ December 1997 in Kyoto, Japan, and entered into force on 16 February 2005 [208]. According to Kyoto protocol all the countries and states under the protocol are given a certain period of time in which they are expected to reduce the volume of greenhouse gases (GHG) with a certain percentage. For an example US had agreed to reduce their greenhouse gas emissions by 5.2% on average for the period 2008-2012 [208]. The most emphasized GHG's by Kyoto protocol are: carbon dioxide, methane, nitrous oxide and sulphur hexafluoride [208]. Although the emitters of the GHG's are both anthropogenic and natural sources, the major contributor is human activities. Therefore fighting climate change requires a development of new technologies and scientific solutions.

## 1.7 The objective of the study

Synthesis of supported gold catalysts is a condition dependent process as reproducibility of these catalysts is hard or rarely achieved. This study investigates the synthesis of gold catalysts via the deposition-precipitation (DP) method.

It is known that catalytic activity of gold catalysts is partly dependent on the synthesis. Therefore, this study intends to investigate the optimal synthesis condition of these catalysts. As such the best suited conditions such pH, aging, calcination temperature and weight loading will be explored. Further, the catalysts that are produced will be characterised thoroughly to understand the structure of the materials.

In order to evaluate the effect of the support material on gold catalysts, the use of different support material will also be undertaken. In this study both reducible and non reducible support will be explored.

In order to overcome particle sintering of gold catalysts at high temperatures, palladium metal will be incorporated such that a bimetallic catalyst is produced. It is therefore proposed that palladium will bring about perturbation to the gold's electronic structure to improve catalytic activity of gold at high temperatures. Bimetallic catalysts will be prepared via simultaneous deposition-precipitation (DP).

The catalytic evaluation both monometallic and bimetallic catalysts will be undertaken. The reaction of interest will be CO oxidation. The prepared catalysts will be subjected to high temperature in order to identify optimum catalytic temperature which the catalysts can sustain. Also to calculate CO to $CO_2$ conversion and deactivation of the catalysts by monitoring time on stream.

Properties of the prepared catalysts will be studied by various techniques. Transmission electron microscopy (TEM) and high resolution electron microscopy (HRTEM) will be utilized for particles size analysis as well as morphology. Powder x-ray diffraction (XRD) will be employed to obtain information about crystallite size and catalyst phase composition. Surface

area of the catalysts will be determined by Brunauer-Emmett-Teller (BET). The metal content on the support will be determined by inductively coupled plasma-optical emission spectrometer (ICP-OES). CO-Temperature programmed desorption (TPD) measurements were carried out to evaluate CO desorption.

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