

CHAPTER II

LITERATURE REVIEW

Until the end of the 1980s, only very limited attention has been paid to catalysis with gold metal because of its electronic configuration of noble metal, which is usually accompanied by very low activities. This situation has been changed in recent years with the discovery of the catalytic activity of gold nanoparticles. Gold catalysts have attracted growing interest due to their potential applicabilities for many reactions of both industrial and environmental importance. The most remarkable catalytic properties of supported gold have been first obtained for the reaction of CO oxidation at subambient temperature by Haruta and co-worker in 1987. When gold is highly dispersed on reducible metal oxide such as TiO_2 , $\alpha\text{-Fe}_2\text{O}_3$, Co_3O_4 , MnO_x and ZrO_2 with diameters smaller than 5 nm, it turns out to be surprisingly active for the low temperature catalytic oxidation of carbon monoxide. For example, gold catalysts supported on Fe, Co, and Ni oxides are able to oxidize CO even at 195 K (Iizuka *et al.*, 1999).

It has been clearly demonstrated that supported gold nanoparticles can be very active catalysts for a variety of reactions in chemical processing, the oxidation of carbon monoxide and hydrocarbons under mild conditions, selective hydrogenation, water-gas shift, reduction of NO with hydrocarbons, epoxidation of propylene, CO and CO_2 hydrogenation, and in reactions involving halogens. Moreover, it is relevant to fuel cell technology and pollution control applications, including odour and poisonous gas abatement in rooms, aircraft and submarines as shown in Table 2.1.

2.1 Chemical and Physical Properties of Gold

Gold (Au) is unique among metallic elements because of its highly resistance to oxidation and corrosion. Physical properties of gold are shown in Table 2.2. It lies in Group 11(IB) of the periodic classification of the elements with copper and silver, which these three metals are often being referred to as the "coinage metals", and lies between platinum in Group 10 and mercury in Group 12. The

predominant oxidation states for gold are Au (I) and Au (III) but the Au (III) state is more stable than Au (I). Gold exhibits all the expected properties of metal in terms of luster, hardness, ductility (ability to be drawn into wire), malleability (ability to be beaten or rolled into sheets), and high thermal and electrical conductance. It has the highest electronegativity especially when compared to selenium, and being only slightly more electropositive than sulfur and iodine.

Table 2.1 Potential applications for gold catalysts (Editorial, 2003)

Heterogeneous	
<i>Chemical processing</i>	WGS; hydrocarbon reactions relevant to petroleum reforming; selective oxidation reactions, including some in the liquid phase; hydrogenation and dehydrogenation reactions
<i>Clean energy generation</i>	Hydrogen purification and electrocatalysts for fuel cells
<i>Environmental pollutions control</i>	Air conditioning in automobiles, aircraft, ships, submarines, trains, office buildings hospitals, factories, restaurants
<i>Waste incinerators</i>	Removal of dioxins
<i>Automotive pollution control</i>	For low temperature applications in diesel vehicles and for cold start with gasoline engines
<i>Sensors</i>	For inflammable and poisonous gases such as hydrocarbons and CO, respectively
Homogeneous	
<i>Chemical processing</i>	Alkyne reactions and selective routes to specialty chemicals such as pharmaceuticals and fragrances

The high electronegativity of gold gives rise to another unique feature of its chemistry. Gold does not react directly with other electronegativity elements such as oxygen, and it is only dissolved in hydrochloric acid when a strong oxidizing agent such as nitrile ion is present (Bond and Thompson, 1999).

Table 2.2 Physical and chemical properties of gold

Property	Value
atomic number	79
atomic mass	196.96655
electronic configuration	[Xe]4f ¹⁴ 5d ¹⁰ 6s ¹
Structure	fcc
melting temperature (K)	1337.33
boiling temperature (K)	3129
specific gravity (at 20 °C)	3081
atomic radius (Å)	1.442 (in the element) 1.35 (in compound)
van der Waals radii (Å)	1.66
ionic radii (Å)	0.71 (+5, c.n. = 6, octahedr.) 0.82 (+3, c.n. = 4, square-planar) 0.99 (+3, c.n. = 6, octahedr.) 1.51 (+1, c.n. = 6, octahedr.)
hardness (eV)	5.6 (Au ⁺) 8.4 (Au ³⁺)

2.2 Gold as a Catalyst

The catalytic performance of Au can be defined by four major factors: particle size, contact structure, supporting material and promoter type. These are important properties for creating a good catalyst.

2.2.1 Particle Size

The remarkable catalytic behavior shown by gold depends on forming it into very small particles. It is generally accepted that the presence of small Au particles (2-15 nm), stabilised by metal oxides, is indispensable to obtain high catalytic performance. The critical diameter of Au particles is 2 nm. When Au particles are smaller than 2 nm, they behave different than bulk Au, and more like Pt or Pd. This critical diameter corresponds with a layer of 3 or 4 atoms thick on the support. This is because the massive metal and large particles cannot chemisorb typical reactant molecules to any useful extent; this only occurs when an adequate number of low-coordination surface atoms are present, ideally on particles so small that they lack full metallic character.

The Au-particles size can be controlled by the catalysts pre-treatment and catalysts preparation method. It was found that Au catalyst particles were found to become larger with an increase in calcination temperature and to change in their shape from round to irregular facing. (Tsubota *et al.*, 1998). Therefore, a low calcination temperature is required to convert the Au precursor into the catalytically active species. The optimum pre-treatment temperature depends on the nature of the support, due to difference in the strength of interaction between Au (precursor) and the support.

2.2.2 Contact Structure

The Au particles are definitely not uniform in size, and the Au crystallites are formed in a variety of contact angles depending on the technique used to deposit Au nanoparticles. All kinds of crystallite morphologies are thinkable, in which the correlation between surface area, or perimeter length, and particle diameter are completely different. Contact of Au particles with the support is very important because the perimeter interfaces around the Au particles act as a site for reaction. The deposition-precipitation method yields hemispherical particles which are strongly attached to the support at their flat planes. In contrast, the impregnation method gives spherical particles simply on top of the support. This difference in contact angle is responsible for more activity of the catalyst because of the interaction with the support material (see Figure 2.1).

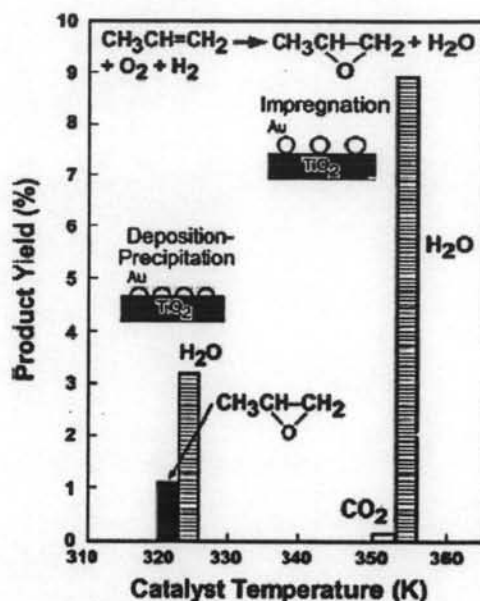


Figure 2.1 Product yields of the reaction among propylene, O₂ and H₂ over Au/TiO₂ catalysts, prepared by deposition-precipitation (left) and impregnation method (right) (Haruta *et al.*, 2001).

2.2.3 Supporting Material

The presence of small Au particles alone cannot explain the catalytic behaviour of Au catalysts; the identity of the supporting material should also be considered important. The selection of the supporting material depends on the reaction that is going to be performed. For oxidation reaction, highly dispersed Au particles supported on reducible metal oxide has received a lot of attention because it exhibits a strong metal-support interaction effect. The reason is the ability of the oxygen migration of reduced support particles on to the surface of metallic particles. For example, many (not too strong acidic) metal oxides, especially semi-conductive metal oxide like TiO₂ and Fe₂O₃ can be used for CO-oxidation reactions. Among single metal oxides, only TiO₂ makes gold selective for the reaction.

2.2.4 Promoter Type

Alkaline and alkaline earth metal oxides (Li₂O, Rb₂O, MgO and BaO) function as a good promoter in the total oxidation of C₃H₆. They are not directly

responsible for high catalytic activity but they can induce a decrease in the size of Au particles which give the higher catalytic performance. In addition, the catalytic activity of Au/Al₂O₃ in C₃H₆ oxidation and carbon monoxide oxidation are improved by the addition of transition metal oxides (TMOs) which exhibit synergetic behavior. These additives can act as a structural promoter and/or a cocatalyst. The Au particles are stabilized against sintering which is that of a structural promoter by increasing the concentration of the active sites. In addition, it was proved experimentally that the lattice oxygen of the oxide plays an active role in oxidation reaction via the Mars and van Krevelen mechanism (Gluhoi *et al.*, 2005).

2.3 Preparation of Active Gold Catalysts

The support and the method of preparation highly affect the activity. The nature of the Au precursors, the method to introduce Au to the support (e.g. coprecipitation, deposition, precipitation, and impregnation) and the pH are variables worth mentioning. These variables will affect particle size, the particle shape and the amount of residual chloride in the catalyst.

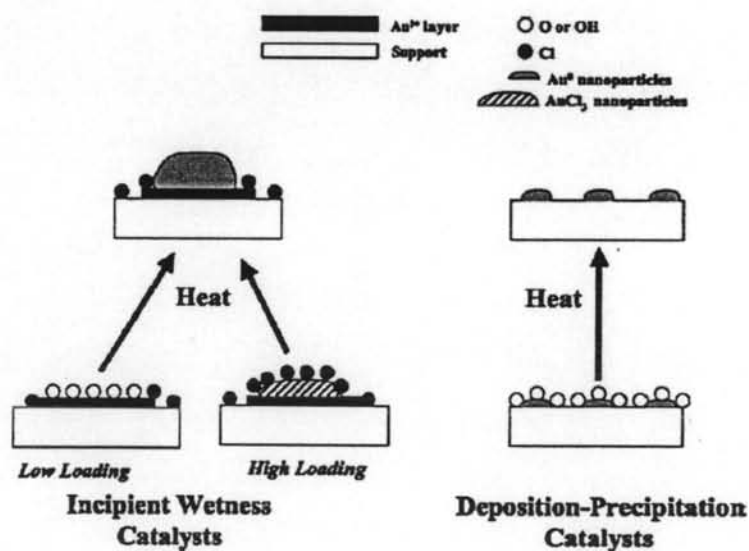


Figure 2.2 Effect of preparation and heating on the gold catalysts (Soares *et al.*, 2003).

Conventional preparation techniques, such as wet impregnation and pore volume impregnation of the support, result in much larger Au particles than co-precipitation or deposition precipitation as shown in Figure 2.2. In addition, the particle size is controlled by the calcination temperature during preparation. At too high temperatures Au particles coagulate with each other or occur sintering.

2.4 Titanium Dioxide or Titania Support

Supported metal catalysts are undoubtedly one of the major areas of research in heterogeneous catalysis. The reducible metal oxide is one of the most important supports which provides a strong metal-support interaction (SMSIs) particularly, titanium dioxide (TiO_2) or titania support. It has been known that titanium dioxide exhibits a strong metal-support interaction effect with group VIII noble metals.

Titanium dioxide is a n-type semiconductor and a typical photocatalyst, attracting much attention from both fundamental and practical viewpoints. It has been used in many industrial areas including environmental purification, solar cell, gas sensors, pigments and cosmetics. To explore novel approaches for the nanostructured titania of various nature with the control of the particle size in nanometer-scale and the morphology is quite interesting, since the performance of titania in its various applications depends on its crystalline phase state, dimensions and morphology.

Titanium dioxide is a lustrous silver-white metal that occurs naturally in three crystalline modifications; anatase (tetragonal), rutile (tetragonal), and brookite (orthorhombic). The last one is not common. Calcination of titanium salts at moderately low temperatures form predominantly anatase, which is converted to rutile at high temperatures around 880 °C. Rutile is the thermally stable form at all temperatures, but conversion of anatase to rutile is so slow that it may be unimportant in most catalytic reactions. Anatase typically has a higher surface area than rutile. Surface area in the range of about 10 m^2/g to 50 m^2/g (Degussa P-25) are available.

Table 2.3 Typical physical and mechanical properties of titania

Properties	Value
Density	4 g / cm ³
Porosity	0%
Modules of Rupture	140 Mpa
Compressive Strength	680 Mpa
Poisson's Ratio	0.27
Fracture Toughness	3.2 Mpa / m ^{1/2}
Shear Modulus	90 Gpa
Modulus of Elasticity	230 Gpa
Microhardness (HV 0.5)	880
Resistivity (25 °C)	10 ¹² ohm·cm
Resistivity (700 °C)	2.5 x 10 ⁴ ohm·cm
Dielectric Constant (1 MHz)	85
Dissipation factor (1 MHz)	5 x 10 ⁻⁴
Dielectric strength	4 kV / mm
Thermal expansion (RT-1000 °C)	9 x 10 ⁻⁶
Thermal Conductivity (25 °C)	11.7 Wm / K

Typically, fumed titania consists of a mixture of anatase and rutile, the ratio varying somewhat with the manufacturing process. Degussa P-25 is report to be about 85 to 90% anatase, 10 to 15% rutile (Satterfield, 1991). Physical and mechanical properties of sintered titania are summarised in Table 2.3.

The discovery of carbon nanotubes in 1991 has drawn extensive research on the synthesis of nanotubes made of materials other than carbon. Nanotubular materials are of great interest because of their exceptional electronic and mechanical properties. Considerable efforts are being devoted to develop novel, well-structured, porous, high surface area and complex forms of TiO₂-based materials. Titanium oxide nanotubes are anticipated to have great potential for use in the preparation of

catalysts, adsorbants and deodorants with high activities owing to their very high specific surface area and uniformity. Since the titanium oxide nanotubes have been found to be rather stable during thermal treatment, their application as catalysts or as supports for catalytic metal particles dispersion seems quite attractive (Idakiev *et al.*, 2005).

2.5 Catalytic Performance of Gold

2.5.1 Oxidation of Carbon Monoxide

Gold-based catalysts have been shown to have the best low-temperature activity for CO oxidation of all catalysts and at low temperature. When Au is highly dispersed on reducible metal oxide such as MnO_x , TiO_x , FeO_x and CoO_x with diameter between 2 and 10 nm in size, it turns out to be surprisingly active for the low temperature catalytic oxidation of carbon monoxide. Anyway, for this reaction most intensively studied is Au supported on TiO_2 . This is because neither Au nor TiO_2 alone is active for CO oxidation but their combination generates surprisingly high catalytic activity (Haruta, 2004). This reaction is of great interest in terms of the purifying of indoor and in-vehicle air, and a large number of studies have been conducted.

The mechanism of CO oxidation over Au/ TiO_2 catalysts was proposed in Figure 2.3. CO oxidation takes place mainly on the perimeter interface of gold particles. For the first step, CO is adsorbed on either surface or perimeter sites of gold to form the carbonyl species, while O_2 is adsorbed on the Au/ TiO_2 surface, most likely on the perimeter interface. Therefore, the reason why supported Au catalysts properly prepared are surprisingly active for CO oxidation can be explained in term of the size effect of Au particles due to an increase in step edge, and corner sites. The carbonyl species on the perimeter site reacts with the O_2 adsorbate so that the O-Au-CO complex and CO_2 are produced. The complex is decomposed also to produce CO_2 . The third step is considered to be the rate determining one. The decoration model proposed in connection with so called "strong metal support interaction" is not applicable to supported Au catalysts.

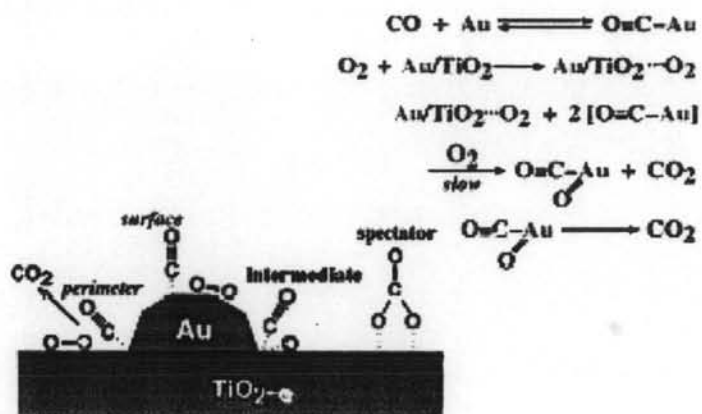


Figure 2.3 A schematic representation of CO oxidation pathways over supported Au catalysts (Haruta, 2004).

2.5.2 Selective Oxidation of Hydrocarbons

The selective oxidation of hydrocarbons, comprising alkanes, alkenes and aromatics, is an important chemical technology for the conversion of oil-and natural gas-based feedstocks to value added products such as oxygenates, which are used as key intermediates for polymer and organic synthesis. The oxidation of alkanes to alkanols and of olefins to epoxides as well as the direct hydroxylation of aromatics have been considered difficult to achieve.

2.5.2.1 *Epoxidation of Propylene*

Propylene oxide (PO) is an important chemical intermediate for chemicals like propylene glycol and polyurethanes which are used to manufacture commercial products like adhesives, paints, and cosmetics (Yap *et al.*, 2004). In 1998, Hayashi and co-worker found that Au supported on TiO₂ (Degussa, P-25) could catalyze the epoxidation of propylene in the gas phase containing O₂ and H₂. Propylene oxide was produced with high selectivity greater than 90% and the propylene conversions of 1-2% at atmospheric pressure and temperatures of 303-393 K when gold highly dispersed and was deposited on TiO₂ by deposition-precipitation techniques as hemispherical particles with diameters smaller than 4.0 nm. Small

hemispherical Au particles will form strongly contact with a TiO_2 particle at their flat planes. It appears that the strong contact of Au particles with the TiO_2 support, giving longer distance of the perimeter interface, is indispensable for the epoxidation of propylene.

The mechanism of the epoxidation of propylene over supported Au catalysts has not been solved yet. However, Clerici and Ingallina (1998) have proposed the mechanism of C_3H_6 epoxidation over Au/ TiO_2 catalysts following mechanistic scheme in Figure 2.4. Over Au/ TiO_2 catalytic system an equilibrium state between $\text{Ti}^{4+}\text{O}-\text{Au}^0 \leftrightarrow \text{Ti}^{3+}-\text{O}-\text{Au}^+$ is likely to be present at the perimeter interface of Au and TiO_2 support. Molecular oxygen is taken up by a Ti^{3+} cation site and is activated, probably to a negatively charged molecular oxygen species, which forms hydroperoxo- or peroxy- like species directly through reaction with hydrogen. Presumably, this is the active oxygen species that reacts with C_3H_6 to form propylene oxide. The key role of Au appears to be in providing binding sites for C_3H_6 and to aid electron transfer from H_2 to O_2 .

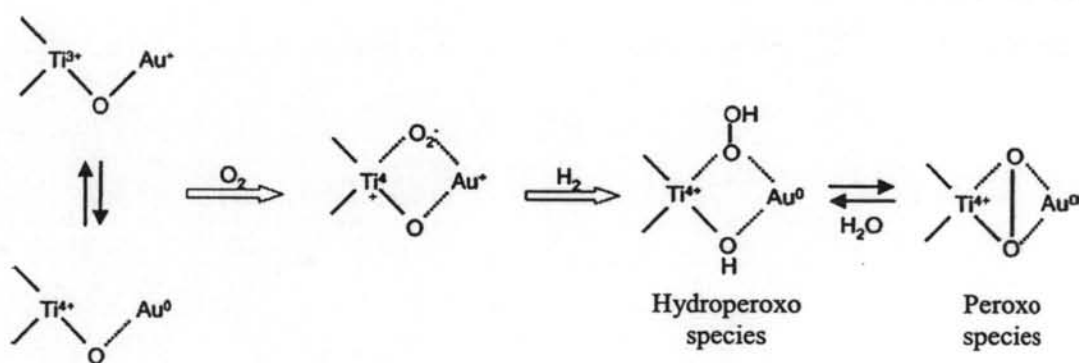


Figure 2.4 Probable mechanism for the formation of the active oxygen species on Au/ TiO_2 catalysts (Monnier, 2001).

2.5.2.2 Total Oxidation of C_3 Hydrocarbons and Volatile Organic Compounds (VOCs)

Gold-based catalysts exhibit catalytic activity for wide range of different reactions including total oxidation of hydrocarbon and volatile organic

compounds for air pollution control propose. These compounds are emitted from many industrial processes and transportation activities. It has been reported that Au/TiO₂ catalysts prepared by impregnation method exhibit complete oxidation of propylene to H₂O and CO₂ (Hayashi *et al.*, 1998). Moreover, Au/iron oxide catalysts present a high activity towards the catalytic oxidation of VOCs. The catalytic behavior of this system has been found to be dependent on preparation method and pre-treatment conditions used. The high activity of Au/Fe₂O₃ catalysts has been explained on the basis of the capacity of gold to increase the mobility of the iron oxide lattice oxygen which is involved in the VOCs oxidation through a Mars-van Krevelen mechanism (Minicò *et al.*, 2000).

2.5.3 Water-Gas Shift Reaction

The water gas shift (WGS) reaction, $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$, is widely used in industry, primarily to generate H₂. Generally, Fe- or Cu-based catalysts are used. However, Au catalysts are also active for the WGS reaction and can exceed the available commercial catalysts in activity. Obviously H₂ is involved in the WGS reaction, but details of its interaction with gold nanoparticles is controversial, claiming evidence that the particles could dissociate H₂, and others claiming that the clusters have a negligible affinity for H₂ and will not disassociate it (Cortie *et al.*, 2002).

Owing to the possible applications of polymer electrolyte fuel cells to automobiles and to residential electricity-heat delivery systems, low-temperature water-gas-shift reaction is attracting renewed interests. In comparison with commercial catalysts based on Ni or Cu, which is operated at 900K or at 600 K, respectively, supported Au catalysts appear to be advantageous in operation at a temperature as low as 473 K. During the course of investigation on the hydrogenation of CO₂ over supported Au catalysts, it was found that Au/TiO₂ was selective to the formation of CO, namely, reverse water-gas-shift reaction at a temperature as low as 473K. Later, Au/TiO₂ was confirmed to be active for water-gas-shift reaction.

2.6 Literature Survey

The previous work related to activity study of Au catalysts in oxidation reaction both CO and hydrocarbons oxidation as well as the other correlated reactions. Moreover, effect of preparation method, calcination temperature and supporting materials were summarized in this section.

The contact angle of gold particles on the support which depend on the preparation method is one of the main effects on activity of Au-based catalysts. Bamwanda and co-worker (1997) reported that the preparation method influence the catalytic activity for CO oxidation. The deposition-precipitation (DP) method gives the most active catalysts for both Pt and Au supported on TiO_2 when compares with photodeposition (FD) and impregnation (IMP). Gold catalysts prepared by DP are active at temperature below 273 K and show a much greater activity than Pt catalysts. DP can produce small Au particles and give high dispersion of Au where as FD and IMP yielded much larger particles and with a poor dispersion. Furthermore, DP is remarkably sensitive larger by four times than Au-IMP and Au-FD. These effects cause from DP can produce hemispherical Au particles which have their flat planes in good contact with TiO_2 , yielding the longest perimeter interface, whereas impregnation and photodeposition give spherical particles which are simply loaded on the metal oxide support. In 1998, the result was confirmed by Tsubota *et al.* They found that Au/ TiO_2 prepared by deposition-precipitation method exhibited very highly catalytic activity for low temperature CO oxidation. It is because Au doposite on TiO_2 as hemispherical fine particles with diameters smaller than 4 nm and it has a stronger interaction between the Au particles and the TiO_2 support. However, in the same year Hayashi and co-worker (1998) reported that a large (several tens nm in diameter) spherical Au particle simply mixed with smaller TiO_2 particles resulted in complete oxidation to H_2O and CO_2 .

Additionally, catalytic activity of Au is influenced from calcination temperature. It is because size of Au particles will become larger with an increase in calcianation temperature. In 2001, Boccuzzi and co-workers studied the effect of calcination for three Au/ TiO_2 catalysts prepared by the deposition-precipitation

technique. The different calcination temperatures were 473, 573 and 873 K giving the mean diameter of Au particles of 2.4, 2.5 and 10.6 nm, respectively. The first two catalysts exhibited 100% conversion of CO at temperature below 240 K, whereas the third catalyst exhibited 100% conversion at temperature above 300 K. Haruta *et al.* (1993) concluded that small Au particles not only provided the sites for the reversible adsorption of CO, but also appreciably increased the amount of oxygen adsorbed on the support oxides. Nevertheless, Tsubota *et al.*, (1998) reported the interesting results of effect of calcination temperature on the catalytic activity of Au colloids mechanically mixed with TiO₂ powder for CO oxidation. The gold catalyst prepared from this method composed of spherical gold particles on TiO₂ support with mean diameter of 5.1 nm when calcine at 473 K. It is poorly active for CO oxidation at temperatures up to 473 K. The catalytic activity appreciably increases with an increase in calcination temperature up to 873 K even though Au particles grow to larger ones and are accompanied by changes in their shape from round to irregular facing. It can be ascribed to the formation of stronger interaction between two phases. A strong contact should be indispensable for the genesis of high catalytic activity for CO oxidation.

The supporting material is one of the considerable effects in activity of gold-based catalysts. Mallick *et al.*, (2003) studied the catalytic activity of CO oxidation over gold nanoparticles supported on TiO₂ and TiO₂-ZnO. They found that introducing ZnO onto TiO₂ caused the surface modification of TiO₂ and was associated with a negative effect on the catalytic activity. It means a superior catalytic activity is achieved when only TiO₂ alone acts as the support. In 2004, Gaşior and co-worker studied the catalytic behavior of Au on various oxide supports catalysts in oxidation of CO, propane and propene and reported that it depends mainly on the nature of the support. The catalysts with transition metal oxides, TMO (Fe, Ti, Ce) as supports were considerably more active in the CO oxidation than those with oxides of main group elements, MGO (Mg, Si, Sn) supports. Oxidation of propane gives carbon oxides as only reaction products at temperatures higher than 250 °C for both catalyst supports. Propene oxidation (in the presence of H₂) gives oxygenated products (mainly propanal and ethanal) on Au supported on oxides of

main group elements at temperatures higher than 150 °C, whereas catalysts with transition metal oxides perform in these conditions mainly total combustion. Propene oxides, as the main reaction product was observed only at low temperatures (< 150 °C) for catalysts containing Ti in the support with the yield of ~1%. No clear correlations have been observed between the activity of the catalysts in the oxidation reactions and reducibility of the catalysts studied by H₂ TPR, nor the dominating Au particle size. In addition, epoxidation of propylene using hydrogen and oxygen over Au particles on various modified titanium silicalite-1 (TS-1) was studied by Yap *et al.*, (2004). Au/TS-1 catalysts prepared by deposition-precipitation method achieved propylene conversions of 2.5-6.5% and propylene oxide selectivities of 60-80% at 443 K, with dilute Au and Ti catalysts exhibiting good stability. A critical Au particle diameter of 2-5 nm is essential for propylene oxide activity, their results are consistent with molecular located near Ti sites inside the TS-1 pores or on the external surface active for propylene epoxidation. The stability of the Au/TS-1 catalyst is highly dependent on Au and Ti loading. Furthermore, titanium oxide nanotubes (TNTs) synthesized via the reaction of TiO₂ crystalline powders of either anatase or rutile phase and NaOH aqueous solution was used as a support in test of water-gas shift reaction (WGSR). Idakiev *et al.*, (2005) showed that gold based catalysts on titanium oxide nanotubes support prepared by deposition-precipitation (DP) method gave an active behavior in water-gas shift reaction at wide temperature range (140-300 °C).

Gold-based catalysts are widely used in many reactions especially, low temperature oxidation of CO and epoxidation of propylene also water-gas shift reaction. Moreover, they are used in catalytic combustion of volatile organic compounds (VOCs) for air pollution control propose and total oxidation of C₃ hydrocarbons also. Scirè and Minicò (2000, 2003) reported that Au/Fe₂O₃ and Au/CeO₂ catalysts prepared by coprecipitation (CP) and deposition-precipitation (DP) have been found to be very active in the oxidation of tested volatile organic compounds (2-propanal, methanol and toluene). The high activity of these systems has been related to the capacity of highly dispersed Au to weaken the surface Fe-O and Ce-O bond adjacent to gold atoms, thus enhancing the mobility of the lattice

oxygen which is involved in the VOCs oxidation through a Mar-van Krevelen reaction mechanism. In 2005, Gluhoi and co-worker found that Au/Al₂O₃ catalysts with the addition of alkali (earth) metal oxides (MO_x, with M = Li, Rb, Mg, or Ba) exhibited the high performance in total oxidation of propene (C₃H₆). It was found that MO_x acts as a promoter and helps to induce a decrease in the size of Au particles and stabilizes them against sintering.