

# Gold as a Novel Catalyst in the 21st Century: Preparation, Working Mechanism and Applications

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**Gold can be deposited as nanoparticles on a variety of support materials by coprecipitation or deposition-precipitation of Au(OH)<sub>3</sub>, grafting of organo-gold complexes such as dimethyl-Au(III)-acetylacetonate, mixing of colloidal Au particles, and vacuum deposition. Owing to the moderate adsorption of at least one of reactants (for example, CO) on the edges and corners of Au nanoparticles and to the activation of the counter reactant (for example, O<sub>2</sub>) at the perimeter interface with the supports, supported Au nanoparticle catalysts exhibit unique and practically useful catalytic properties at relatively low temperature below 473K. They have already been commercially used for deodorizers in rest rooms in Japan and will find growing applications in indoor air quality control, pollutant emission control, production of hydrogen energy carrier, and innovations in chemical processes. Cluster science of Au may also open an exciting area of research showing some magic numbers for dramatic changes in reactivity.**

## Introduction

Historically, gold was regarded to be catalytically inert, but since the discovery of surprisingly high catalytic activity for low-temperature CO oxidation (1), it has been shown that gold becomes active for many reactions when stabilized in the form of nanoparticles attached to metal oxide and activated carbon supports (2-5). In the 1990's, R&D activity on the catalysis of Au tended to grow appreciably (3). This paper focuses on recent advances, especially in the techniques for preparing highly dispersed Au catalysts, a working mechanism for CO oxidation, and potential applications and future prospects.

## Preparation of nanoparticulate Au catalysts

It is difficult to deposit Au as nanoparticles on metal oxide supports by impregnation methods mainly because Au has a lower melting point and a lower affinity for metal oxides than Pd and Pt. Another reason is that during calcination of HAuCl<sub>4</sub> crystallites which are dispersed on the support surfaces, chloride ion markedly enhances the coagulation of gold particles. As summarized in Table 1, there are four categories of techniques that can lead to the deposition of Au nanoparticles with diameters below 10 nm (6). It is very important to choose a suitable technique depending on the kind of support materials such as basic or acidic metal oxides, carbonaceous materials, or single crystals.

The first category is characterized by the preparation of well-mixed precursors, for example, hydroxide, oxide, or metal mixtures of Au with the metal component of the support by coprecipitation (7), amorphous alloying (11) or co-sputtering (12), respectively. These precursor mixtures are then transformed during calcination in air at temperatures above 550K into metallic Au particles strongly attached to the crystalline metal oxides such as  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>, and NiO.

Among the three techniques, coprecipitation is the most useful and simplest method of preparation. An aqueous solution of HAuCl<sub>4</sub>•4H<sub>2</sub>O and water soluble metal salts, most preferably nitrates, such as Fe(NO<sub>3</sub>)<sub>2</sub>•9H<sub>2</sub>O is poured into an aqueous alkaline solution under agitation for a few minutes. After ageing for 1 hour, the precipitates are washed with water for more than 5 times and filtered. The hydroxide and/or carbonate mixture is dried overnight and calcined to obtain powder catalysts. What are important to obtain homogeneous dispersion of Au nanoparticles can be summarized as follows.

- 1) Concentrating of metal salts solution: 0.1-0.4M/l.
- 2) Neutralizer: Na<sub>2</sub>CO<sub>3</sub> or K<sub>2</sub>CO<sub>3</sub>

Since gold hydroxide, Au(OH)<sub>3</sub>, is amphoteric, its solubility

**Table 1**

Preparation Techniques for Nanoparticulate Gold Catalysts

Categories	Preparation techniques	Support materials	Ref.
Preparation of mixed precursors of Au and the metal component of supports	coprecipitation (hydroxides or carbonates) CP	Be(OH) <sub>2</sub> , TiO <sub>2</sub> *, Mn <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> , Co <sub>3</sub> O <sub>4</sub> , NiO, ZnO, In <sub>2</sub> O <sub>3</sub> , SnO <sub>2</sub>	1, 7, 8, 9, 10
	amorphous alloy (metals) AA	ZrO <sub>2</sub>	11
	co-sputtering (oxides) in the presence of O <sub>2</sub> CS	Co <sub>3</sub> O <sub>4</sub>	12
Strong interaction of Au precursors with support materials	deposition-precipitation (HAuCl <sub>4</sub> in aqueous solution) DP	Mg(OH) <sub>2</sub> *, Al <sub>2</sub> O <sub>3</sub> , TiO <sub>2</sub> , Fe <sub>2</sub> O <sub>3</sub> , Co <sub>3</sub> O <sub>4</sub> , NiO, ZnO, ZrO <sub>2</sub> , CeO <sub>2</sub> , Ti-SiO <sub>2</sub>	13, 14
	liquid phase grafting (organogold complex in organic solvents) LG	TiO <sub>2</sub> , MnOx, Fe <sub>2</sub> O <sub>3</sub>	15, 16
	gas phase grafting (organogold complex) GG	all kinds, including SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub> , and activated carbon	17, 18
Mixing colloidal Au with support materials	colloid mixing CM	TiO <sub>2</sub> , activated carbon	19, 20
Model catalysts using single crystal supports	vacuum deposition VD (at low temperature)	Defects are the sites for deposition, MgO, SiO <sub>2</sub> , TiO <sub>2</sub>	21, 22, 23

\* The addition of Mg citrate during or after coprecipitation or deposition-precipitation is important for depositing Au as nanoparticles.

increases due to the formation of Au(OH)<sub>4</sub><sup>-</sup> anion when the pH is too high. Therefore, precipitation is most efficient in the pH range of 7-10. When metal salt solution is added to Na<sub>2</sub>CO<sub>3</sub> or K<sub>2</sub>CO<sub>3</sub> solution, precipitate can be formed at a relatively constant pH. When NaOH solution is used, its pH inevitably changes during coprecipitation. The use of NH<sub>4</sub>OH solution usually results in the formation of Au particles larger than 10 nm in diameter. However, it has recently been reported that ageing for several hours leads to small Au nanoparticles when homogeneous precipitation using urea as a neutralizer is applied (24).

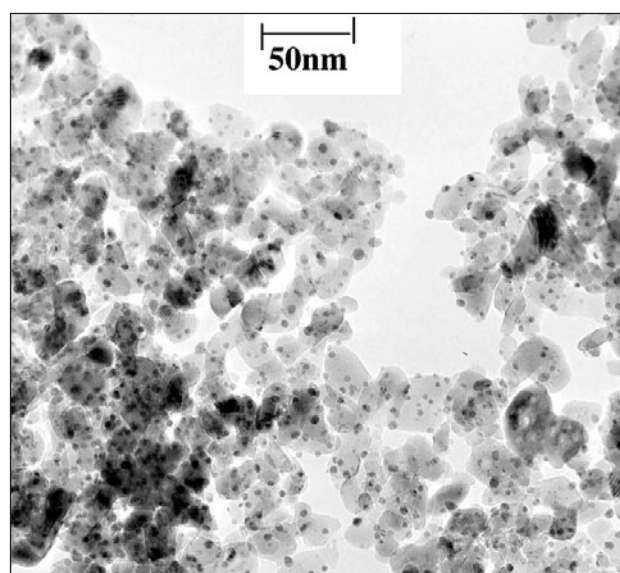
3) Temperature: 320-360K for precipitation and 550-670K for calcination

Aqueous solutions for coprecipitation should be warmed to a temperature in the range of 320-360K to promote the exchange of chloride from the AuCl<sub>4</sub><sup>-</sup> ion with OH. In the case of Au/Co<sub>3</sub>O<sub>4</sub>, coprecipitation should be carried out in the temperature range of 270-300K for the sake of depressing the reduction of AuCl<sub>4</sub><sup>-</sup> ion with the oxidation of Co<sup>2+</sup> ion to Co<sup>3+</sup> ion. The catalytic activity for low-temperature CO oxidation of coprecipitates reaches a maximum when they are calcined in air at temperatures above 550K, where Au hydroxide species mostly change to metallic Au particles (8). Above 670K, the sintering of Au nanoparticles becomes accelerated.

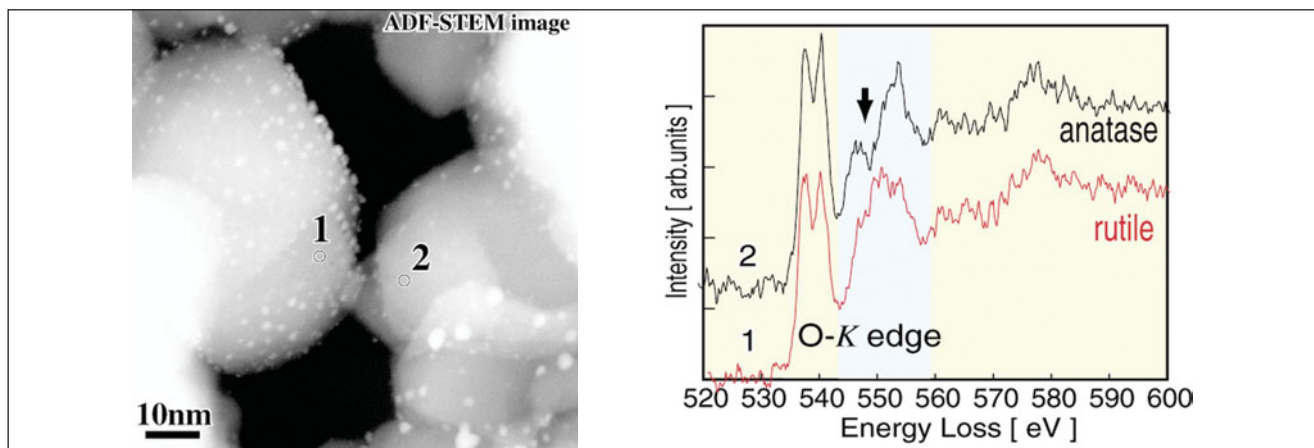
Figure 1 shows a TEM photograph for Au/α-Fe<sub>2</sub>O<sub>3</sub> prepared by coprecipitation. Gold nanoparticles are homogeneously dispersed on α-Fe<sub>2</sub>O<sub>3</sub> particles, with a standard deviation of the diameter of about 30%. The applicability of coprecipitation is limited to metal hydroxides or carbonates that can be coprecipitated with Au(OH)<sub>3</sub>.

Actually, Au can be supported in the form of well-dispersed nanoparticles on α-Fe<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>, NiO, and ZnO while not on TiO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, MnOx, and CdO (7). In the case of TiO<sub>2</sub>, the addition of Mg citrate during or after coprecipitation results in a good dispersion (9), while in the case of Mn<sub>2</sub>O<sub>3</sub>, precipitation with LiCO<sub>3</sub> solution leads to better catalytic activity for CO oxidation in a hydrogen stream (10).

The second category is based on the deposition or adsorption of Au compounds, for example, Au hydroxide by deposition-precipitation (DP) (13) or an organogold complex by liquid phase grafting (LG) (15,16) and by gas phase

**Figure 1**

TEM photograph for Au/α-Fe<sub>2</sub>O<sub>3</sub> prepared by coprecipitation followed by calcination at 673K

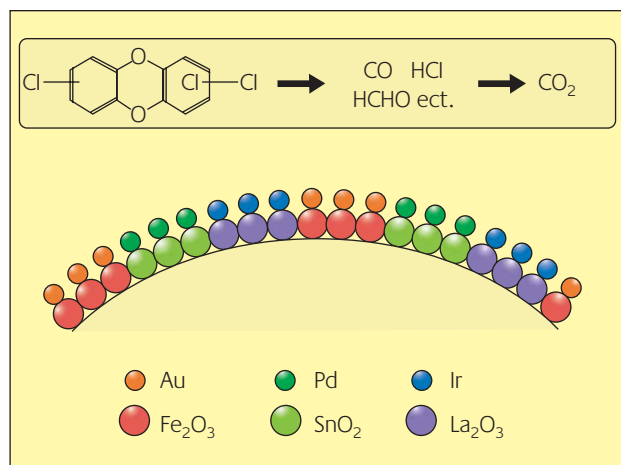


**Figure 2**  
ADF-STEM and EELS analyses for Au/TiO<sub>2</sub> (p-25) prepared by deposition-precipitation

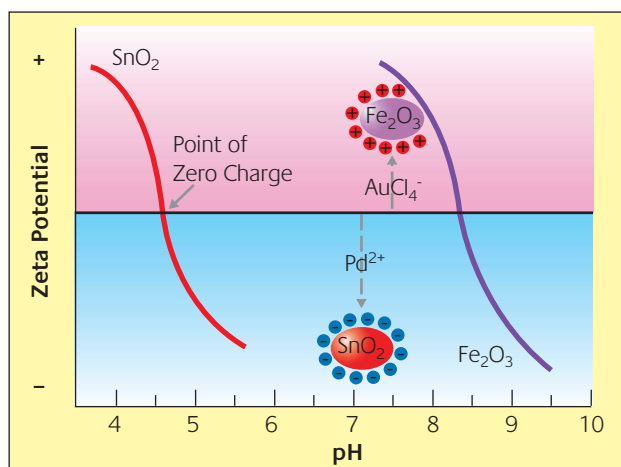
grafting (GG) (17). The DP method is the easiest to handle and is used for producing commercial Au catalysts. Due to the amphoteric properties of Au(OH)<sub>3</sub>, the pH of aqueous HAuCl<sub>4</sub> solution is adjusted at a fixed point in the range of 6 to 10, and is selected primarily based on the isoelectric points (IEP) of the metal oxide supports. Careful control of the concentration around 10<sup>-3</sup>M/l, with the pH in the range of 6 to 10, and the temperature in the range of 323K to 363K of the aqueous HAuCl<sub>4</sub> solution enables selective deposition of Au(OH)<sub>3</sub> only on the surfaces of the support metal oxides without precipitation in the liquid phase. Because the precursor can be washed before drying, Na and Cl ions are removed to a level of a few tens ppm. As in the case of coprecipitation, the removal of Cl<sup>-</sup> ions by washing can avoid the coagulation of Au nanoparticles.

The only constraint of DP is that it is not applicable to metal oxides, the IEPs of which are below 5, and to activated carbon. Gold hydroxide cannot be deposited on SiO<sub>2</sub> (IEP=2), SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (IEP=1), or WO<sub>3</sub> (IEP=1). Liquid phase grafting in organic solvent has also the same constraint and furthermore it needs freshly prepared metal hydroxides (15), probably because the concentration of surface OH groups should be high enough for the interaction with organo-gold complexes. In contrast, by using dimethyl-Au(III)-acetylacetonate (25), GG is unique because it can deposit Au nanoparticles on almost all kinds of supports, for example, SiO<sub>2</sub> and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, and activated carbon (18).

The third category is to use monodispersed Au colloids stabilized by organic ligands or polymer compounds (19,20). Among the former six techniques, only GG is effective for depositing Au nanoparticles on activated carbon, but the sizes of Au particles are relatively large (around 10 nm). Precise control of dispersion and size (within 5 nm in diameter) of Au nanoparticles can be accomplished by dipping Au sols stabilized with polyvinyl pyrrolidone or tetrakis(hydroxymethyl)phosphonium chloride (20).



**Figure 3**  
Schematic representation of a multi-functional catalyst integrating three supported precious metal catalysts, Pd/SnO<sub>2</sub>, Ir/La<sub>2</sub>O<sub>3</sub> and Au/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>



**Figure 4**  
Schematic drawing for the selective deposition of Pd on SnO<sub>2</sub> and of Au on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>

In the preparation of model catalysts, on single crystals of MgO and TiO<sub>2</sub> (rutile), size selected Au anion clusters can be deposited with homogeneous dispersion at relatively low temperatures (21,23). Surface defects or specific surface cages are suggested as sites for stabilizing the Au clusters (21,22).

By utilizing the pH dependency of Au deposition in DP, Au nanoparticles can be deposited on a specific site of support materials or on a specific kind and crystallite of metal oxide mixtures. When TiO<sub>2</sub> powder (Degussa P25) which had been considered to be composed of anatase and rutile was used as a support, as shown in Figure 2, Au particles were deposited densely on one group of TiO<sub>2</sub> particles whereas they were rarely deposited on another group of TiO<sub>2</sub> particles (26). TEM observation and EELS spectra proved that Au particles were deposited on rutile but not on anatase, revealing that P25 TiO<sub>2</sub> was composed of two types of crystalline particles, not of a homogeneous or surface-covered mixture in one single particle.

In the case of TiO<sub>2</sub> deposited on SiO<sub>2</sub> and titanosilicates where titanium cations are incorporated as isolated species in the matrix of SiO<sub>2</sub>, DP leads to the selective deposition of Au nanoparticles on TiO<sub>2</sub> or isolated Ti cation sites, not on SiO<sub>2</sub> surfaces. This structure is indispensable for the selective epoxidation of propylene using gas streams containing O<sub>2</sub> and H<sub>2</sub> (27). The same catalytic system prepared by GG which enables the non-selective deposition of Au particles both on TiO<sub>2</sub> and SiO<sub>2</sub>, is not selective at all for the epoxidation of propylene.

In future applications gold catalysts may be used in combination with other precious metal catalysts and base metal oxide catalysts, especially in environmental pollutant abatement. We have demonstrated that the most effective approach is to integrate a few different supported nanoscale precious metal catalysts, as schematically shown in Figure 3. The idea is to combine synergistically the different performances of each precious metal by choosing the most suitable support for a target reaction and then by integrating them into a single catalytic system. An integrated catalyst composed of Pd/SnO<sub>2</sub>, Ir/La<sub>2</sub>O<sub>3</sub>, and Au/Fe<sub>2</sub>O<sub>3</sub> exhibited enhanced catalytic activities not only for dioxin decomposition but also for the oxidation of H<sub>2</sub> and (CH<sub>3</sub>)<sub>3</sub>N (28).

A mixture of SnO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> was prepared by coprecipitation from an aqueous solution of SnCl<sub>4</sub> and Fe(NO<sub>3</sub>)<sub>2</sub>, followed by calcination in air at 673K. Figure 4 shows a guiding principle for the selective deposition of Pd and Au. Palladium was first deposited by DP from an aqueous solution of Pd(CH<sub>3</sub>COO)<sub>2</sub> at pH=7, where the Pd<sup>2+</sup> cation could approach negatively charged SnO<sub>2</sub>, but was not allowed to approach Fe<sub>2</sub>O<sub>3</sub> which is positively charged. After washing and calcination at 673K, the sample composed of PdO/SnO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> was aged in an aqueous solution of HAuCl<sub>4</sub> at

pH7.5. Gold hydroxide Au(OH)<sub>3</sub> was then selectively deposited from Au(OH)<sub>n</sub>Cl<sub>4-n</sub><sup>-</sup> anion on the positively charged Fe<sub>2</sub>O<sub>3</sub>, without precipitation on the negatively charged SnO<sub>2</sub>. After washing and calcination, the sample composed of PdO/SnO<sub>2</sub> and Au/Fe<sub>2</sub>O<sub>3</sub> was dispersed in an aqueous solution of Na<sub>2</sub>CO<sub>3</sub>, to which an aqueous solution of IrCl<sub>4</sub> and La(NO<sub>3</sub>)<sub>3</sub> was poured to obtain finally a mixture of Pd/SnO<sub>2</sub>+Ir/La<sub>2</sub>O<sub>3</sub>+Au/Fe<sub>2</sub>O<sub>3</sub> through washing, calcination, and reduction in H<sub>2</sub> stream.

## Structure Sensitivity of CO Oxidation

Except for H<sub>2</sub> oxidation and hydrocarbon hydrogenations, most reactions are remarkably structure-sensitive over supported Au catalysts. The oxidation of CO is the simplest reaction and has been the most intensively studied (29). This reaction is practically important in the purification of engine exhaust gases and of hydrogen produced by steam reforming of methanol and hydrocarbons for polymer electrolyte fuel cells (10). The oxidation of CO over Au catalysts is remarkably sensitive to the contact structure between the Au particles and the support, the type of support, and the size the Au particles.

### 1) Contact Structure of Gold Particles

Table 2 lists the turnover frequencies (TOFs), the reaction rates over one single surface metal atom per second, of CO oxidation at 300K over Pt/TiO<sub>2</sub> and Au/TiO<sub>2</sub> catalysts prepared by DP, photochemical deposition, and IMP methods (30). The DP method yields hemispherical metal particles with their flat planes strongly attached to the TiO<sub>2</sub> support, often by epitaxial contact, Au (111) to anatase TiO<sub>2</sub> (112) and rutile TiO<sub>2</sub> (110), while photocatalytic deposition and IMP methods yield spherical particles, which are simply loaded on the TiO<sub>2</sub> support and, therefore, are much larger, particularly in the case of Au. Over Pt/TiO<sub>2</sub>, the reaction of CO with O<sub>2</sub> takes place preferentially on the Pt surfaces and the metal oxide support is less involved in the reaction. This can explain why different methods of preparation do not make any appreciable difference in the TOF of Pt catalysts. In contrast, the TOF of Au/TiO<sub>2</sub> markedly depends on the methods of preparation and varies by four orders of magnitude. The TOF of strongly attached hemispherical Au particles exceeds that of Pt by one order of magnitude. The dramatic difference in TOFs suggests that the contact structure is the most critical factor in supported Au catalysts.

The sharp contrast between the above two precious metal catalysts in CO oxidation suggests that the reactions might take place at the perimeter interfaces around the Au particles. To confirm this hypothesis, Vannice prepared an inversely supported catalyst, namely, TiO<sub>2</sub> layers deposited on

**Table 2**CO oxidation over Pt/TiO<sub>2</sub> and Au/TiO<sub>2</sub> prepared by different methods (30)

Metal	Preparation methods	Metal loading (wt%)	Diameter of Au (nm)	T <sub>1/2</sub> * (K)	Rate at 300K (mol s <sup>-1</sup> g-cat <sup>-1</sup> )	TOF at 300K (s <sup>-1</sup> )	Ea (kJ/mol)
Pt	DP	1.0	1.3 ± 0.3	334	1.4 × 10 <sup>-7</sup>	2.7 × 10 <sup>-3</sup>	49
	IMP	1.0	1.4 ± 0.3	339	1.9 × 10 <sup>-7</sup>	3.8 × 10 <sup>-3</sup>	60
	PD	0.9	2.4 ± 0.6	363	2.4 × 10 <sup>-8</sup>	9.2 × 10 <sup>-3</sup>	53
Au	DP	0.7	3.1 ± 0.7	282	6.9 × 10 <sup>-7</sup>	3.4 × 10 <sup>-2</sup>	19
	DP	1.8	2.7 ± 0.6	253	5.5 × 10 <sup>-6</sup>	1.2 × 10 <sup>-1</sup>	18
	IMP	1.0	10<_	481	1.7 × 10 <sup>-10</sup>	—	58
	PD	1.0	4.6 ± 1.5	477	1.5 × 10 <sup>-10</sup>	9.6 × 10 <sup>-6</sup>	56

\*T<sub>1/2</sub> : temperature for 50% conversion of 1 vol% Co in air under a space velocity of 2 × 10<sup>4</sup>h<sup>-1</sup>. ml/g-cat. Preparation methods : DP deposition precipitation, IMP Impregnation, PD photochemical deposition.

a Au substrate, and observed appreciable catalytic activity (31). We have prepared a Au/TiO<sub>2</sub> catalyst by mechanically mixing a colloidal solution of 5 nm diameter Au particles with TiO<sub>2</sub> powder, followed by calcination in air at different temperatures (32). Calcination at 873K promotes the sintering of Au particles and the formation of larger particles with diameters above 10 nm, but at the same time, with stronger contact (observed by TEM) leading to much higher catalytic activity than at 573K.

## 2) Kind and Crystalline Type of Metal Oxide Support

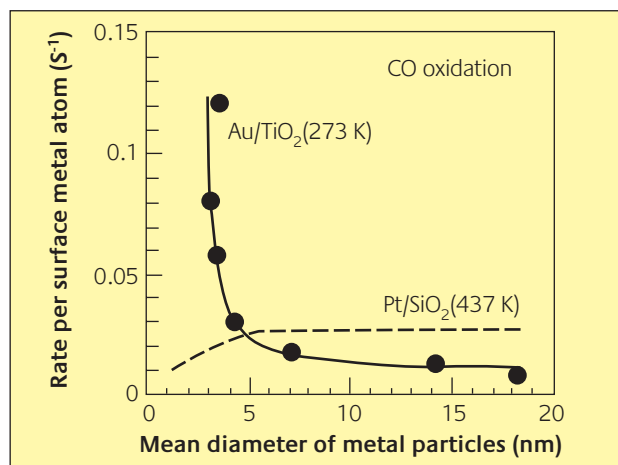
For CO oxidation, many oxides other than strongly acidic materials such as Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> and activated carbon can be used as a support and induce activity even below 300K. For Pd and Pt, semiconductor metal oxides lead to enhanced catalytic activities but at temperatures above 300K. Semiconductive metal oxides such as TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, and NiO provide more stable Au catalysts than do insulating metal oxides such as Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>. Among Au supported on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, or TiO<sub>2</sub>, the TOFs at room temperature under a moisture level of around 10 ppm are nearly equal, indicating that the contributions of the metal oxide supports are more or less similar in intensity (33). The difference appears in the moisture effect: Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> require a concentration of H<sub>2</sub>O of at least 10 ppm higher than that for TiO<sub>2</sub>, for CO oxidation to proceed at room temperature (34). Alkaline earth metal hydroxides such as Be(OH)<sub>2</sub> and Mg(OH)<sub>2</sub> are excellent choices for demonstrating high activity at a temperature as low as 196K (35,36). In contrast, when an acidic material such as Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, WO<sub>3</sub>, or activated carbon is used as a support, gold exhibits poor activity; even at temperatures above 473K the conversions are far below 100% (33).

Low-temperature CO oxidation under an acidic environment has not yet been accomplished by any means. This reaction is very important in relation to polymer

electrolyte fuel cells, which are operated at relatively low temperatures of around 373K (37). In order to use methanol directly as a fuel, the anode should also be active for the electrochemical oxidation of CO. However, the present Pt electrode is not only inactive but also deactivated. Low-temperature CO oxidation under an acidic environment is a critical issue in opening a new stage of fuel cell development.

## 3) Size of the Au Particles

Figure 5 plots the TOFs of CO oxidation over Pt/SiO<sub>2</sub> and Au/TiO<sub>2</sub> as a function of the mean diameter of metal particles. A sharp increase in the TOF is observed with a decrease in the diameter from 4 nm. In contrast, the Pt group of metals shows a decreasing or steady TOF (38). The rates over Au/TiO<sub>2</sub> were about one order of magnitude greater when measured as the temperature was lowered from 353K than when measured as the temperature was raised from 203K (4,39). This difference is assumed to occur from the accumulation of carbonate species on the surfaces of the support at low temperatures resulting in the loss of the

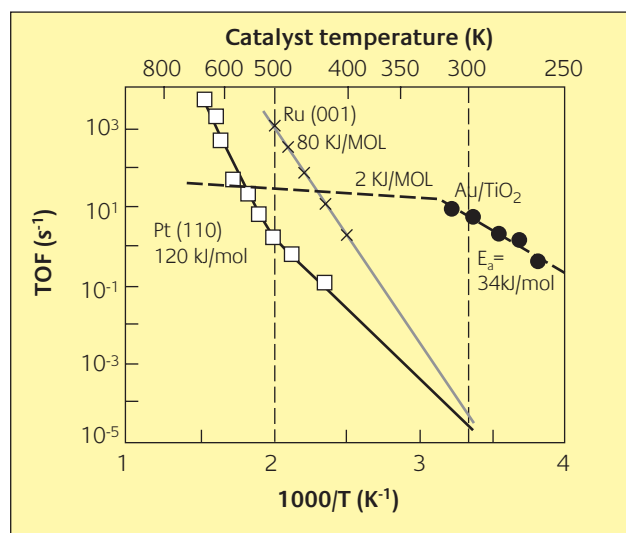
**Figure 5**Turnover frequency (TOF) for CO oxidation over Pt/SiO<sub>2</sub> and Au/TiO<sub>2</sub>

activating power of the perimeter interfaces for  $O_2$ . Therefore, the rate over  $Au/TiO_2$ , which was deactivated during experiments at lower temperatures, can be regarded as close to the rate of the CO reaction with  $O_2$  over the surfaces of the Au particles without the contribution of  $O_2$  activation at the perimeter interfaces. The one order of magnitude difference in the rate between fresh (obtained by high temperature measurements) and deactivated  $Au/TiO_2$  can be ascribed to the contribution of the  $TiO_2$  support. Accordingly, the increase in the TOF can be explained if the adsorption sites for CO are edge, corner, or step sites, and the reaction zone is the periphery around the Au particles, the proportions of which increase in hemispherical Au particles with a decrease in their size (40).

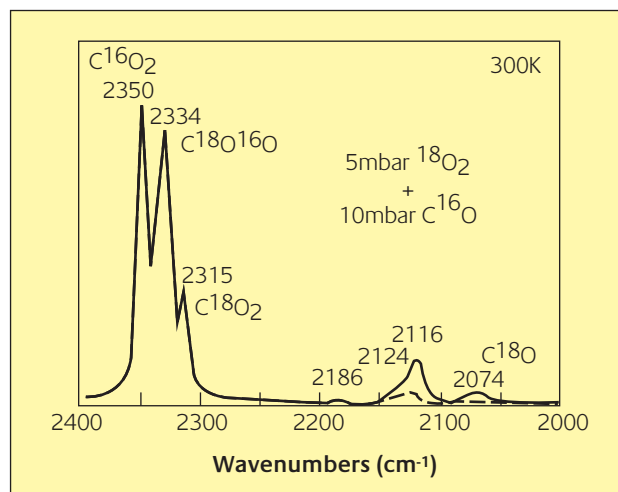
## Kinetics and Reaction Mechanism of CO Oxidation

Figure 6 shows Arrhenius plots for CO oxidation over noble metal catalysts. A unique feature of Au catalysts is that apparent activation energies ( $E_a$ ) are very low. At temperatures below 300K, the value of  $E_a$  is 20 to 40 kJ/mol and is nearly zero at temperatures above 300K. In contrast, Pt group metals have a value of  $E_a$  ranging from 50 kJ/mol (Table 2) to 170 kJ/mol (41) and are more active than Au but only at temperatures above 500K. At room temperature, Au is more active by 1-4 orders of magnitude.

The rate of CO oxidation over  $Au/TiO_2$ ,  $Au/Fe_2O_3$ ,  $Au/Co_3O_4$  is independent of the concentration of CO and is slightly dependent on the concentration of  $O_2$  (on the order of 0 to 0.25) (42). Over unsupported Au powder with mean



**Figure 6**  
Arrhenius plots of the turn-over frequency (TOF) for CO oxidation over noble metal catalysts. The data for Pt group metals are taken from ref. [41]



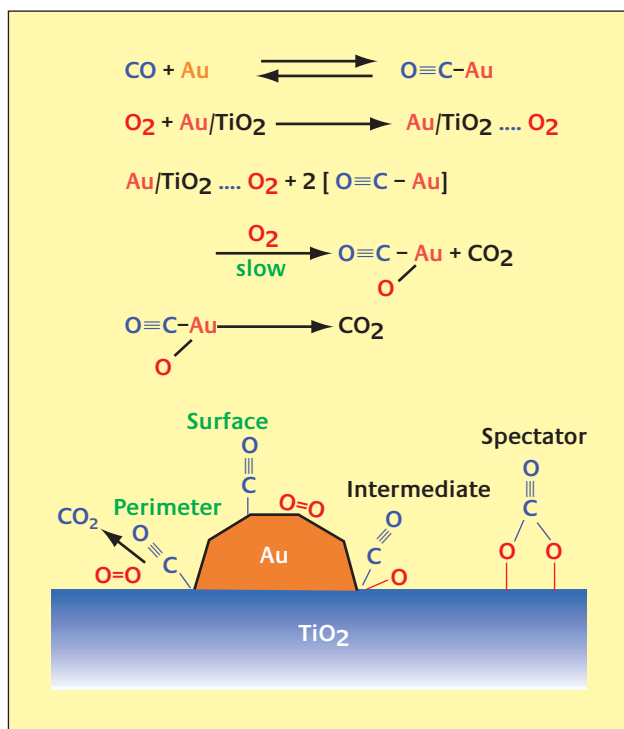
**Figure 7**  
FT-IR spectra for the introduction of  $C^{16}O$  at 300 K to  $Au/TiO_2$  after preadsorption of  $^{18}O_2$

diameters of 17 nm, the rate is almost independent of the concentrations of CO and  $O_2$  (39). This independence suggests that CO and  $O_2$  are adsorbed on the catalyst surfaces nearly to saturation and that the reaction of the two adsorbed species is the rate-determining step.

In FT-IR spectra for CO adsorption at 90K over  $Au/TiO_2$  calcined in air at different temperatures (43), the most active sample (calcined at 573K, with Au particles having a mean diameter of 2.4 nm) exhibits the largest peak intensities, at 2110 to 2120  $cm^{-1}$ . This can be attributed to the linear adsorption of CO on the metallic Au sites (44). When the diameter of the Au particles becomes larger than 10 nm (sample calcined at 873K), the intensity of the peak is markedly reduced, indicating that CO adsorption might only occur on the steps, edges, and corners of the Au particles and not on the smooth surfaces. This agrees well with what has previously been discussed based on the self-consistent density functional theory calculations by Mavrikakis et al (40).

No direct experimental evidence has yet been presented showing that oxygen is activated for reacting with CO adsorbed on the Au surfaces or for whether oxygen molecule is dissociatively or non-dissociatively adsorbed. A TAP (temporal analysis of products) study of  $O_2$  adsorption and the reaction of  $O_2$  with CO (45,46),  $^{18}O_2$  isotope experiments (43,45,46), and ESR measurements (47,48) indicate that molecularly adsorbed  $O_2$ , most likely  $O_2^-$  at the perimeter interface, is involved in the oxidation of CO. Figure 7 shows FT-IR for the introduction of  $C^{16}O$  at 300K to  $Au/TiO_2$  preadsorbed with  $^{18}O_2$  (43). That  $C^{16}O_2$  is formed in a quantity comparable to that of  $C^{16}O^{18}O$  means that the oxygen species ( $^{16}O$ ) contained in the surface layer of the  $TiO_2$  support is also involved in CO oxidation at room temperature.

There are other arguments as well regarding the active species of Au, especially in the case of  $Au/Fe_2O_3$ . These include



**Figure 8**  
Probable pathways for CO oxidation over supported Au catalysts

oxidized Au species, Au<sup>+</sup> (49), Au<sup>δ+</sup> (50), or metal oxide support surfaces with modified reducibility by the interaction with Au nanoparticles (51,52). It is unlikely that oxidic Au species are the major catalytically active phases because the most active supported Au catalysts are prepared by calcination in air at 573K, where Au precursors (hydroxides or organo complexes) are mostly transformed into metallic particles. A certain fraction of Au species remain as atomically dispersed species in the matrix of the support, as proved by EXAFS (8,50,53,54), XPS (51), Mössbauer (52,55), and IR of CO adsorbed (43,49).

**Table 3**  
Ongoing and potential applications of Au catalysts

Fields of applications	Reactants or Reactions	Support materials
Indoor air quality control	odour (commercialized), CO sick house gases	Fe <sub>2</sub> O <sub>3</sub> TiO <sub>2</sub>
Pollutant abatement	dioxin oxidation-decomposition NO reduction N <sub>2</sub> O decomposition	Fe <sub>2</sub> O <sub>3</sub> Al <sub>2</sub> O <sub>3</sub> Co <sub>3</sub> O <sub>4</sub>
H <sub>2</sub> energy carrier	water-gas shift CO removal fuel cell anode	ZrO <sub>2</sub> , CeO <sub>2</sub> Al <sub>2</sub> O <sub>3</sub> , Mn <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> carbon black
Chemical process	hydrochlorination hydrogenation [C=C, C=O + C=C, C-OH] liquid-phase selective oxidation propylene epoxidation	AuCl <sub>3</sub> / activated carbon ZnO  activated carbon TiO <sub>2</sub> (anatase) and Ti-SiO <sub>2</sub>

However, no correlation between the amount of oxidic Au species and catalytic activity has yet been presented. A reason why the samples primarily consisting of oxidic Au probably exhibited high catalytic activity might be that the oxidic Au species were transformed into metallic particles during reaction or storage of the sample after preparation.

Although metallic Au particles are indispensable, a question arises as to why the periphery of Au particles can activate O<sub>2</sub> molecules at low temperatures. As firstly proposed by Bond and Thompson (56) and later discussed by Kung (57), it is probable that the perimeter interfaces contain oxidic Au species, most probably Au(OH)<sub>3</sub> or Au(OH), under usual conditions wherever H<sub>2</sub>O is present at concentrations above 1 ppm. These hydroxides might be stabilized and reversibly formed and decomposed by the aid of the metal oxide supports.

An argument proposed by Goodman and his coworkers is that the non-metallic nature of Au clusters leads to high catalytic activity (23,58). This conclusion is questionable as far as CO oxidation is concerned. The transition of the electronic state was measured for one specific Au cluster of a defined diameter by scanning tunneling spectroscopy, whereas the catalytic activity was measured for an entire Au/TiO<sub>2</sub> model catalyst specimen with a mean diameter of all Au clusters. A maximum in the catalytic activity with respect to the mean diameter of the Au clusters was observed where the transition of the electronic state of the specific Au cluster occurred from metallic to non-metallic. This result can be more reasonably explained by assuming that metallic Au surfaces are necessary for CO adsorption and that the peripheries act as reaction zones with O<sub>2</sub>. A maximum total surface area or number of step sites (40) of metallic Au clusters is obtained at a thickness of 2 atoms, where the transition to non-metallic state begins.

Based on the above arguments and by taking into account a recent overview (59), the most probable pathway for CO oxidation over supported Au catalysts can be depicted as shown in Figure 8.

## Applications and Future Prospect of Gold Catalysts

Gold catalysts with selected support materials can also promote many reactions other than CO oxidation. Table 3 lists such reactions, which usually take place at much lower temperatures or with much higher degrees of selectivity over Au catalysts than over other metal catalysts (5).

The characteristic features of supported gold catalysts are remarkable structure sensitivity of their catalytic performance, low apparent activation energies (active at low temperatures), and moisture activation. By taking advantages of these properties, R & D efforts on Au catalysts are expected to expand in three directions. The first direction involves the discovery of new capabilities for Au particles larger than 2 nm that are stable up to 673K. Combinations with other metal catalysts might contribute to further develop the capabilities of Au catalysts. Although Ir/La<sub>2</sub>O<sub>3</sub> itself is weakly active, it can effectively enhance the catalytic activity of Pd/SnO<sub>2</sub> and Au/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. The booster effect of Ir catalysts yielded a 95% decomposition of dioxin from the outlet gases of incinerators even at 423K at an hourly space velocity of 12,000h<sup>-1</sup> • ml/g-cat. (28).

The second direction involves application of the mechanism of Au catalysis and the techniques developed for preparing Au catalysts to other noble metals. In most cases, the genesis of the catalysis of Au is ascribed to the perimeter interfaces around the Au particles. This presents us with a new guiding principle for creating a wide range of new catalytic systems, because the combination of catalytic metals with a variety of support materials should present numerous novel catalysts. Some good examples are Pd/CeO<sub>2</sub> and Pt/ZrO<sub>2</sub> prepared by coprecipitation or deposition-precipitation for the low-temperature decomposition and synthesis of methanol (60,61) and for the low-temperature oxidation of CO and reduction of NO (62).

The third direction involves the development of cluster science for Au particles smaller than 2 nm. Fundamental work has recently led to an understanding of the unique catalysis of Au as well as its size- and structure-dependency. Through the use of surface science techniques using well-defined catalytic materials, generally size-selected Au clusters deposited on single crystalline metal oxides such as MgO (63) and TiO<sub>2</sub> (23,58,64,65), an atomic scale perspective is being developed in combination with theoretical calculations (40,66,67). It is also instructive that the catalytic activity

changes dramatically depending on the three-dimensional structure of the 13-atom Au clusters (36). Recently, it has been reported that a 55 atom cluster is specifically inert even against active atomic oxygen species (68). Wang and his coworkers have reported that a 20 atom cluster of tetrahedron structure has a large energy gap between HOMO and LUMO and is more stable than fullerene (69). From this perspective, Au might be the best research target because Au itself is poorly active and detectable catalytic activity and marked change in reactivity is only obtained when the Au particles have a specific structure and size. What is also an advantage in studying Au model catalysts is that the activity can often be observed at lower temperatures where designed structures can be maintained.

To increase the effectiveness of recent attempts to combine experimental work using real and model catalysts with theoretical calculations (70), the effect of moisture should also be considered. Most work in surface science occurs in an ultra high vacuum, while measurements of the activity of real catalysts are conducted in a fixed bed flow reactor using reactant gas containing a moisture level of at least 1 ppm, usually 10 ppm. The catalyst surfaces are covered with OH groups and water molecules at room temperature. For CO oxidation, which does not produce H<sub>2</sub>O and proceeds at temperatures below 373K, moisture markedly changes the catalytic activity of the metal oxides and the Au catalysts. Under dry conditions with an H<sub>2</sub>O concentration of 80 ppb, CO oxidation can occur over Co<sub>3</sub>O<sub>4</sub> without Au even at 210K (71,72), while supported Au catalysts prefer moisture (34,73).

## Conclusions

- 1) There are at least eight techniques for preparing highly dispersed gold catalysts. The catalytic performances of gold catalysts markedly depend on the preparation methods and conditions because the following three factors define the genesis of unique catalysis by gold: strong contact between Au particles and the support, selection of the support, and the size of the Au particles.
- 2) Perimeter interfaces provide the sites for reaction, while metallic Au surfaces are still required as reservoirs for a reactant.
- 3) Very low apparent activation energies and enhancement by moisture contribute to the advantages of using Au catalysts in environmental applications, where low-temperature operation is often preferred.
- 4) Gold is the best example for fundamental studies on the effect of size below 2 nm through model catalysts and theoretical calculations.
- 5) The methods of preparation and the mechanisms that

induce the high catalytic activity of Au are applicable to other metals.

## About the Author

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