

Size- and support-dependency in the catalysis of gold

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Abstract

The adsorption properties and reactivities of gold are summarized in terms of their size dependency from bulk to fine particles, clusters and atoms. The catalytic performances of gold markedly depend on dispersion, supports, and preparation methods. When gold is deposited on select metal oxides as hemispherical ultra-fine particles with diameters smaller than 5 nm, it exhibits surprisingly high activities and/or selectivities in the combustion of CO and saturated hydrocarbons, the oxidation-decomposition of amines and organic halogenated compounds, the partial oxidation of hydrocarbons, the hydrogenation of carbon oxides, unsaturated carbonyl compounds, alkynes and alkadienes, and the reduction of nitrogen oxides. The unique catalytic nature of supported gold can be explained by assuming that the gold–metal oxide perimeter interface acts as a site for activating at least one of the reactants, for example, oxygen. Some examples and future prospects in applications are also briefly described.

Keywords: Gold catalysts; Adsorption; Preparation

1. Introduction

Since gold is the least reactive metal, it has been regarded as poorly active as a heterogeneous catalyst. In the past the catalysis of gold was extensively studied by Bond [1,2] and Paravano [3]. The past work was reviewed by Wachs [4] and Schwank [5,6], who stated that gold had been little used in practical heterogeneous catalysis. Quite recently, the nobility of gold has been theoretically illustrated through the high dissociation energy of hydrogen molecule and the low chemical adsorption energy on the surface [7]. However, we should recall that our knowledge has come from the chemistry of smooth gold surfaces or of rela-

tively large gold particles with diameters above 10 nm.

When gold is deposited on select metal oxides as ultra-fine particles, we have found that its chemistry dramatically changes [8]. Highly dispersed gold catalysts are really very active in many important reactions for chemical industry and environmental protection and have already been used for commercial applications in offensive odor removal [9] and gas sensors [10]. As in the case of heterogeneous catalysis, the electrochemistry of gold in aqueous media appears to be interesting too and is considerably more complex than is normally assumed [11,12]. The present paper deals with an overview of the recent achievements in supported gold catalysts.

Specific emphasis is put on the characteristic features of gold in contrast to noble metals of group VIII.

2. Adsorption on gold surface

Gold is inert towards most molecules, however, as shown in Table 1, its surface reactivity appreciably changes with structure. At room temperature only HCOOH, H₂S and thiol compounds can adsorb on the smooth surface of Au. The strong affinity of gold for sulfur is applied to gas sensors using evaporated films of Au for the detection of H₂S [34] and other sulfide

compounds. Recently, molecular electronics [36] and self-assembly [37,38] also utilize the specific bonding between Au and sulfur-containing functional groups. The clean gold surface has been proved to be hydrophilic [32,33]. Gold surfaces scratched by ceramic needles can adsorb hexane compounds, benzene, ethers and ketones [39]. Olefins like ethylene and acetylene are adsorbed on gold evaporated on a substrate as separated islands [13,31].

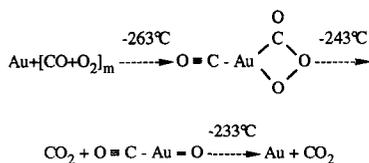
Oxygen does not adsorb on clean Au(110) and (111) surfaces [15], however, atomic oxygen can be formed when gold is exposed to excited di-oxygen produced on a hot filament [17], in an electric discharge [15] or microwave

Table 1
Adsorption of gas molecules on gold surface (See also Refs. [4,13–38])

Molecules	-100	0	100	200	300	Ref.
O ₂	thin film	×	×	×	Au/MgO, Al ₂ O ₃ , SiO ₂	13–22
NO _x	Au(111)					18, 23
N ₂	×	×	×	×	×	13
CO	thin film	Au/TiO ₂ , SiO ₂				24–30
H ₂		×	×	×		13, 29, 30
HCOOH	Au(110) (111)					4, 31
HCHO	×	×	×			4
CH ₃ OH	Au(111) (110)					4, 31
CH≡CH	Au(110)	thin film				13, 31
CH ₂ =CH ₂	Au(110)	thin film				13, 31
H ₂ O						32, 33
H ₂ S						34, 35
Thiols						36–38

-200 -100 0 100 200 300 400
Temperature, °C

Bulk surface,
 Small particles in thin film or powder,
 × No adsorption



Scheme 1. Reactivity of atomic gold.

[22], and to ozone [18]. On relatively clean gold powder prepared by evaporation in inert gas (the diameter of primary particles is about 30 nm, specific surface area 4.1 m²/g), oxygen as well as CO can chemisorb at 0°C [14]. The chemisorbed oxygen on Au has a Brønsted base character as on Ag and Cu and reacts with formic acid, acetylene, and methanol but not with ethylene which is less acidic in the gas phase [15]. It is also reactive with CO even at 0°C to form CO₂ [14,91]. These results suggest that gold can act as a novel oxidation catalyst once oxygen is activated on the defective surface of fine powder or excited by other means. One good example is seen in Au deposited on an inner wall of the quartz tube of a sealed-type recycling CO₂ laser; CO is reoxidized to CO₂ at room temperature only during laser operation [40].

Gold clusters are reactive at room temperature with H₂, CH₄, and O₂ [41]. The reactivity depends on the electrical charge (positive, negative, neutral) and on the atomic number of Au clusters, being observed at specific magic numbers.

Atomic gold is reactive and at an extremely low temperature as -263°C it can react with CO and O₂ according to Scheme 1 [42].

The above results provide evidence that the surface adsorption and reactivity of gold can be tuned by creating defective surface structures through down-sizing or scratching. Because the bonding strength of adsorbates on the defect sites of Au is moderate and still weaker than that on Pd and Pt, it often happens that at low temperatures gold catalysts are advantageous over other noble metal catalysts.

3. Preparation of highly dispersed gold catalysts

Noble metal catalysts are mostly prepared by impregnation methods, which, however, cannot produce active gold catalysts. The impregnation methods can hardly lead to high dispersion of gold except for a few cases of very low metal loadings because of the lower melting point of Au (1063°C) than those of Pd (1550°C) and Pt (1769°C) and partly because the catalyst precursors are often calcined at low temperatures (below 600°C) where chlorine still remains in the metal oxide supports.

The following four methods can deposit gold on a variety of metal oxides as small particles with diameters below 5 nm.

1. Coprecipitation [8]: An aqueous solution of HAuCl₄ and a metal nitrate is poured into an aqueous solution of Na₂CO₃ to obtain a hydroxide or carbonate coprecipitate. The precursor is washed, dried, and finally calcined in air at a temperature above 250°C.
2. Deposition-precipitation [43]: After the pH of an aqueous solution of HAuCl₄ is adjusted to a fixed point in the range of 6 to 10, a metal oxide support in any form, powder, bead, honeycomb, or thin film is immersed in the solution. Aging for about 1 h results in the deposition of Au(OH)₃ exclusively on the surface of metal oxide support if concentration and temperature is properly chosen. The precursor is treated in a similar manner as in coprecipitation. The remarkable influence of the pH on the particle size of Au is shown in Fig. 1 for TiO₂. Above pH 6 main species of Au in solution is transformed from AuCl₄⁻ to Au(OH)_nCl_{4-n} (n = 1–3) and the mean particle diameters of Au in the calcined catalysts become smaller than 4 nm.
3. Co-sputtering [44]: In an atmosphere containing oxygen, gold and metal oxide are simultaneously sputter-deposited on a substrate to form thin film, which is finally annealed in air.
4. Chemical vapor deposition [45]: The vapor

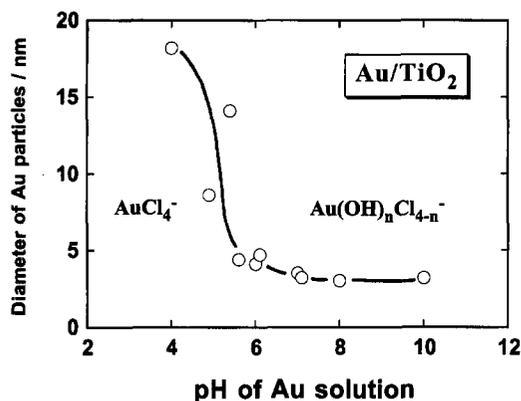


Fig. 1. The mean particle diameter of Au as a function of the pH of HAuCl_4 solution for the Au/TiO_2 catalysts prepared by deposition–precipitation method. Au content in the HAuCl_4 solution corresponded to 13 wt% with respect to TiO_2 . Calcination was done in air at 400°C .

of an organic gold compound, typically dimethyl-gold(III)-acetyl acetonate, is introduced onto an evacuated metal oxide support. The adsorbed organic gold compound is

pyrolyzed in air to decompose it into small gold particles. This method can be applied to a wide variety of metal oxides, while the liquid-phase methods are usually not valid to acidic metal oxides like SiO_2 .

The above four methods can produce hemispherical gold particles (Fig. 2), which are strongly attached to metal oxide supports at their flat planes and accordingly thermally more stable than spherical particles. This can be ascribed to the hydroxidic, oxidic, or organic precursors having stronger affinity to metal oxides. It should also be pointed out that the precursors are washed almost completely or prepared without contamination. In this context, some reported results may not be general because lower activity and deactivation suggest that the samples might be contaminated by Cl^- [46] and Na^+ [47].

Supported gold catalysts prepared by the above methods exhibit unique catalytic perfor-

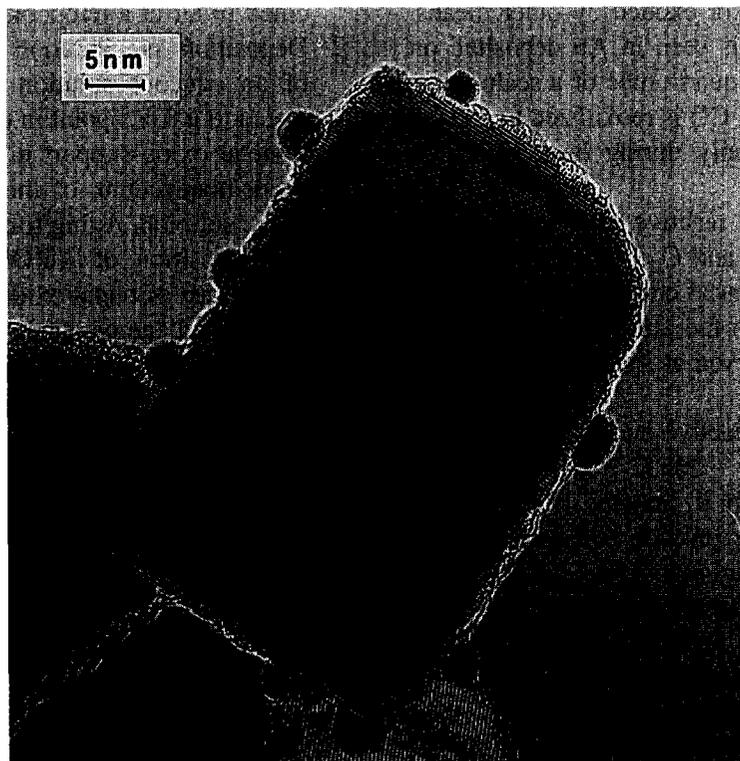


Fig. 2. Transmission electron microscopic photograph for the Au/TiO_2 prepared by deposition–precipitation at pH7. Other conditions were the same as those for Fig. 1.

mances different from unsupported gold and are often more active than Pd and Pt catalysts at low temperatures. Typical examples for CO oxidation are shown in Fig. 3 [48]. While the catalytic activity of Pt/TiO₂ is almost independent of preparation methods, that of Au/TiO₂ changes dramatically. The Au/TiO₂ catalysts prepared by deposition–precipitation are active even at temperatures below 0°C when Au loadings are above 1 wt% and have turnover frequencies larger than those of Pt/TiO₂ by about 1 order of magnitude. This markedly enhanced catalytic activity cannot be fully explained by the size effect of Au particles. Use of a physical mixture of TiO₂ powder with spherical Au particles of diameters around 5 nm calcined in air at different temperatures indicates that the contact structure of gold particles which yields the

longest distance of perimeter interface is important for the genesis of high activity at low temperatures [49].

For CO oxidation, supported gold catalysts should be pretreated in air normally at temperatures above 200°C. Evacuation at 400°C remarkably reduces catalytic activity, which is gradually restored during CO oxidation in the presence of excess oxygen [50]. In contrast, Pt supported on SnO₂, which is also active at room temperature, needs pretreatment in H₂ to form alloys composed of Pt and Sn [51]. This difference suggests that the oxidation of the surface, most specifically, of the perimeter interface between gold and metal oxide support, is important for supported gold catalysts. An FT-IR study showed that CO adsorption was depressed by an evacuation pretreatment at 400°C and that

Table 2
Effective support materials for gold and reactions catalyzed

Reactions	Supports	Notes	Ref.
Complete oxidation			
CO	TiO ₂ , Fe ₂ O ₃ , Co ₃ O ₄ , NiO Be(OH) ₂ , Mg(OH) ₂ Mn ₂ O ₃	active even at –70°C active even at –70°C selective in H ₂ at 80°C	[8,53] [54,55] [56]
CH ₄ (CH ₃) ₃ N	Co ₃ O ₄ NiFe ₂ O ₄	as active as Pd selective to N ₂	[48,57] [9]
Partial oxidation			
CH ₃ CH=CH ₂ → CHOCH=CH ₂	Bi ₂ Mo ₃ O ₁₂	enhanced cat. activity with selectivity unchanged	[58]
CH ₃ CH=CH ₂ → CH ₃ CH(CHO)CH ₂	TiO ₂	highly selective in the presence of H ₂	[59]
C ₃ H ₈ → (CH ₃) ₂ CO	TiO ₂	selective in the presence of H ₂	[59]
i-C ₄ H ₁₀ → (CH ₃) ₃ COH	TiO ₂	selective in the presence of H ₂	[59]
C ₅ H ₁₁ OH → C ₄ H ₉ CHO	borosilicate glass	NO ₂ → NO	[60]
Hydrogenation			
CO ₂ , CO → CH ₃ OH	ZnO, Fe ₂ O ₃ , ZrO ₂	as active as Cu	[61,64]
H ₂ C=CH–CH=CH ₂ → H ₃ C–CH ₂ –CH=CH ₂	Al ₂ O ₃	highly selective	[65,67]
Environmental			
NO + C ₃ H ₆ + O ₂ → N ₂	ZnO, TiO ₂ , Al ₂ O ₃	less selective to N ₂ O	[68]
Decomp. of halogenated compounds	Al ₂ O ₃ , Co ₃ O ₄	longer life than Pt	[69,70]
HCN synthesis from chlorofluorocarbons	LaF ₃	more stable than Pt	[71]
Photocatalytic H ₂ production	TiO ₂	less active by 70% than Pt	[72,73]
Others			
CH≡CH + HCl → CH ₂ =CHCl	HAuCl ₄ /C	highest catalytic activity	[74]

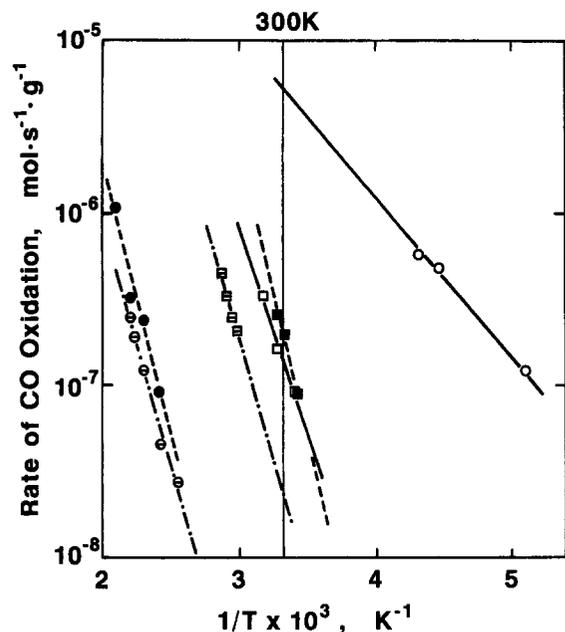


Fig. 3. Logarithmic reaction rate of CO oxidation over Pt-TiO₂ and Au-TiO₂ catalysts as a function of reciprocal temperature. Open square, 1.0%Pt-DP; filled square, 1.0%Pt-IMP; striped square, 0.9%Pt-FD; open circle, 1.8%Au-DP; filled circle, 1.0%Au-IMP; striped circle, 1.0%Au-FD.

after oxidizing pretreatment CO and oxygen can coadsorb on a gold surface at room temperature [52].

4. Catalysis of supported gold particles

The catalytic nature of gold is newly created or tuned by metal oxide supports. For example, in the oxidation of CO and H₂, gold supported on metal oxides other than SiO₂ and Al₂O₃ is much more active for CO oxidation while unsupported gold powder is more active for H₂ oxidation [53]. In many other reactions, as shown in Table 2, excellent catalytic performance by gold can be brought about by the proper selection of support materials.

4.1. Oxidation

4.1.1. Low-temperature catalytic combustion

At present it is only methanol and its decomposed derivatives that can be catalytically oxi-

dized at ambient temperature [75]. For the complete oxidation of MeOH, HCHO, and HCOOH gold supported on TiO₂, α -Fe₂O₃, or Co₃O₄ is almost as active as Pd or Pt supported on Al₂O₃ [56].

The low-temperature activities of supported gold catalysts have recently prompted many groups to work on CO oxidation [76–85] in addition to the previous work using unsupported gold [86–88]. The most effective supports are the oxides of 3d transition metals of group VIII [8,53] and the hydroxides of alkaline earth metals [54,55]. With high Au metal loadings above 10 wt%, these supports make gold active even at a temperature as low as -76°C. It is interesting to note that 3d transition metal oxides allow gold particles to be larger than 2 nm but alkaline earth metal hydroxides require gold particles smaller than 2 nm [89]. For the selective oxidation of CO in H₂, which is required for polymer-electrolyte fuel cell operation, Mn oxides give active and stable catalysts [56].

4.1.2. Mechanism for CO oxidation

The catalytic behavior of gold deposited on metal oxides with different catalytic activities for CO oxidation, TiO₂ (poorly active), α -Fe₂O₃ (active), and Co₃O₄ (very active) can be summarized as follows.

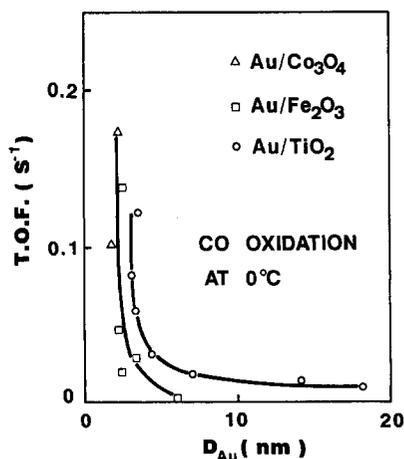


Fig. 4. Turnover frequencies based on surface exposed gold atoms as a function of the mean particle diameters of gold in CO oxidation at 0°C. Δ , Au/Co₃O₄; \square , Au/ α -Fe₂O₃; \circ , Au/TiO₂.

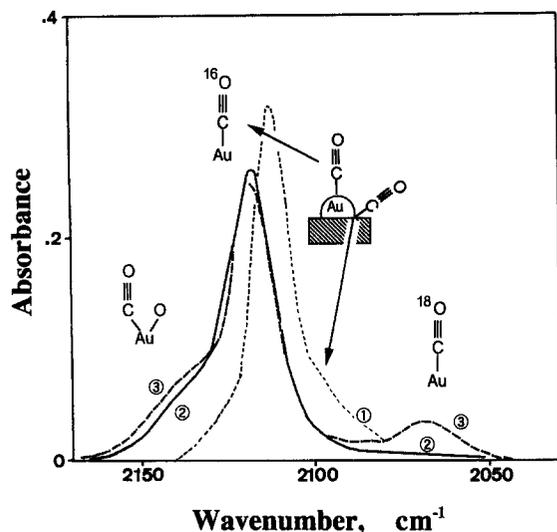


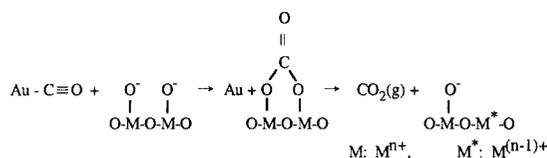
Fig. 5. IR absorption spectra in the carbonyl stretching region produced by different interactions. Curve 1, 0.5 mbar of CO; curve 2, inlet of 0.5 mbar of $^{16}\text{O}_2$; curve 3, inlet of 0.5 mbar of $^{18}\text{O}_2$.

1. The catalytic activity can be correlated with the contact structure giving the longest perimeter distance of gold-support interface [49,53].
2. The turnover frequency increases with a decrease in the mean diameter of gold particles (Fig. 4) [53].
3. The reaction rate is 0 ~ 0.05 order with respect to CO and 0.05 ~ 0.24 with respect to O_2 [53].
4. Moisture enhances the catalytic activity [90].
5. CO is adsorbed as a linearly bonded carbonyl on the surface and perimeter interface of gold particles (Fig. 5) and on the surface of metal oxide support as carbonate and carboxylate species [52]. On introduction of $^{18}\text{O}_2$, oxygen-exchanged carbonyl $\text{Au}-\text{C}\equiv^{18}\text{O}$ and oxygen-coadsorbed $^{18}\text{O}=\text{Au}-\text{C}\equiv\text{O}$ species appear on the surface of gold together with C^{16}O_2 , $\text{C}^{16}\text{O}^{18}\text{O}$, and C^{18}O_2 in the gas phase. The surface carbonates on metal oxide do not include ^{18}O and require a longer time (several minutes) for desorption.
6. Even on unsupported fine gold powder O_2 as well as CO can adsorb and the reaction

between them can also take place at 0°C [91], however, the catalytic activity per unit surface area of Au particles is about 100 times smaller than that of Au/TiO_2 [92].

Based on the above results, the following reaction pathways can be proposed:

1. Reversible adsorption of CO on the surface and perimeter interface of Au: $\text{Au} + \text{CO} \rightarrow \text{Au}-\text{C}\equiv\text{O}$.
2. Irreversible adsorption of O_2 at the perimeter interface: $\text{Au}-\text{TiO}_2 + \text{O}_2 + e^- \rightarrow \text{Au}-\text{O}_2^- - \text{TiO}_2$ (rate-determining).
3. Surface reaction on Au: $\text{Au}-\text{C}\equiv\text{O} + \text{Au}-\text{O}_2^- - \text{TiO}_2 \rightarrow \text{Au}-\text{O}^- + \text{CO}_2(\text{g}) + \text{Au}-\text{TiO}_2$ (on perimeter interface: fast), and $\text{Au}-\text{C}\equiv\text{O} + \text{Au}-\text{O}^- \rightarrow \text{Au} + \text{O}^- - \text{Au}-\text{C}\equiv\text{O} \rightarrow 2\text{Au} + \text{CO}_2(\text{g}) + e^-$ (on Au surface: slow).
4. Surface reaction on the metal oxide:



5. Catalytic combustion of hydrocarbons

Gold deposited on Co_3O_4 exhibits the highest catalytic activity among supported gold catalysts for the complete oxidation (combustion) of hydrocarbon fuels [48,57]. It is inferior to Pd and Pt catalysts in the combustion of unsaturated hydrocarbons like propylene, however, it is as active or more active for saturated hydrocarbons like CH_4 and C_3H_8 . This is probably because olefins can adsorb on the defect sites of small gold particles a little too strongly and may retard the migration of oxygen adsorbed at the perimeter interface. In the case of Pd and Pt, they adsorb olefins much more strongly than Au, however, probably this may make the dissociation of C–C bonding in olefins faster than in alkanes to give higher catalytic activities for olefins.

In the oxidation of trimethylamine, a typical odorous compound, Au/NiFe₂O₄ exhibits the highest catalytic activity at temperatures below 200°C [9]. The advantageous features of the supported gold catalysts over supported Pt catalysts are higher catalytic activity at low temperatures and much higher selectivity to N₂ against N₂O.

6. Selective partial oxidation

In the past it has been reported that partial oxidation took place to form HCHO from CH₄ (Au/BaSO₄, 650°C, yield 0.4%) [93], HCHO from CH₃OH (Au gauze, 450°C, yield 100%) [94], and propylene oxide (Au/SiO₂, yield below 1%, selectivity 50%) [95] or acrolein (Au/SiO₂, 262°C, yield 5%, selectivity 33%) [96] from propylene. However, except for the partial oxidation of CH₃OH, the results could not be reproduced. Gold supported on Al₂O₃ and MgO was reported not to produce ethylene oxide [97] and propylene oxide [98] from the corresponding olefins because of two surface center adsorption per olefin molecule. Gas phase reaction in the absence of catalyst has recently been found to yield oxygenates with similar conversions [99,100].

When Au, Pd, and Pt are supported on Bi₂Mo₃O₁₂, which is an active phase for the partial oxidation of propylene to acrolein, only gold increases the yield of acrolein maintaining selectivity unchanged while Pd and Pt enhance complete oxidation of propylene to CO₂ [58].

Our recent work has revealed that Au/TiO₂ exhibits excellent selectivities in the partial oxidation of propylene, propane, and iso-butane to propylene oxide, acetone, and tert-butanol, respectively, when both oxygen and hydrogen are present [59]. In the partial oxidation of propylene, as clearly shown in Table 3, Au is 100% selective for the partial oxidation to produce propylene oxide while Pd and Pt are selective to hydrogenation to produce propane. The above results indicate that over Pd and Pt hydrogen dissociation takes place preferentially resulting in hydrogenation while over Au hydrogen is activated with surface adsorbed oxygen to form an active and selective oxygen species, most likely hydroperoxo species. It is very striking that the reaction products switch from propylene oxide to propane when the Au loading is lowered to 0.05 wt% from 0.1 wt% [101]. Careful TEM observation suggests a possibility that the switch over of reaction occurs at a critical diameter of gold particles around 2.0 nm (Fig. 6). This implies that gold particles with diameter smaller than 2.0 nm resemble Pd and Pt in the presence of oxygen and can dissociate hydrogen molecules into atomic species. The enhancing effect of O₂ addition in the hydrogenation of propylene to form propane over Au/SiO₂ [102] appears to coincide with the above phenomenon observed for Au/TiO₂.

In the partial oxidation by NO₂, gold supported on borosilicate glass exhibits good selectivities to form aldehydes and ketones from alcohols [60]. The high selectivity to NO from NO₂ is applied to the detection of butylated

Table 3
Reaction of propylene with hydrogen and oxygen over Au-, Pd-, Pt-TiO₂ catalysts

Catalyst	Metal loadings (wt%)	Reaction temperature (°C)	Conversion (%)				Selectivity (%)				PO yield (%)	PO STY ^a (mmol/g-cat/h)
			C ₃ H ₆	H ₂	PO	acetone	C ₃ H ₈	CO ₂				
Au-TiO ₂ ^b	1	50	1.1	3.2	> 99	–	–	–	–	1.09	0.18	
Au-TiO ₂ ^c	1	80	0.2	8.9	–	–	< 10	> 70	0.00	0.00	0.00	
Pd-TiO ₂ ^c	1	25	57.1	97.7	–	0.4	–	–	1	0.00	0.00	
Pt-TiO ₂ ^c	1	25	12.1	86.6	–	2	–	–	6	0.00	0.00	

Feed gas, H₂/O₂/propylene/Ar (10:10:10:70, vol%); flow rate 2000 ml/h; catalysts, 0.5 g.

^a Space time yield.

^b Prepared by deposition-precipitation.

^c Prepared by impregnation.

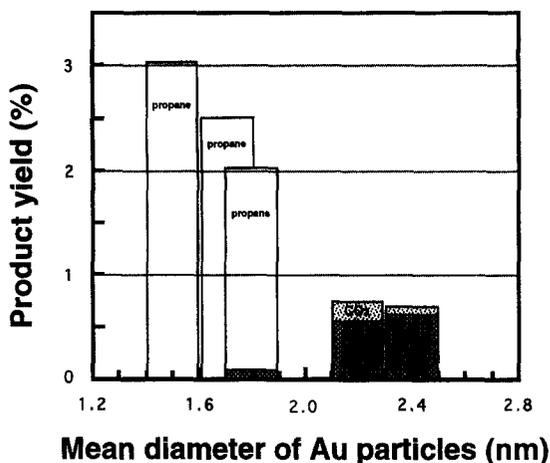


Fig. 6. Product yields for the reaction of propylene with O₂ and H₂ over Au/TiO₂ catalysts as a function of the mean diameters of Au particles. Feed gas, H₂/O₂/propylene/Ar (10:10:10:70, vol%); space velocity 4000 ml/h per g-cat.; reaction temperature 80°C.

hydroxy toluene which is used as an anti-knocking agent for jet fuel [103,104]. Hydrogen peroxide can appreciably enhance the yield of coupling products from CH₄ over a Au/La₂O₃/CaO catalyst [105].

6.1. Hydrogenation

If gold supported on ZnO [61,62] and ZrO₂ [63] is prepared by coprecipitation, it gives methanol in the hydrogenation of CO and CO₂ while other noble metals lead to deep hydrogenation to form CH₄ as a main product. It should also be noted that Au/ZrO₂ prepared from amorphous alloy mainly produces CH₄ from CO [106]. Although commercial Cu/ZnO based catalysts are more active than the above gold catalysts, Cu, Ag, and Au catalysts prepared in Baiker's [63] and our [62] laboratories for comparison under the same conditions (metal loadings and preparation methods) give almost comparable catalytic activity and selectivity to methanol. This result indicates the necessity to recall the proposal presented by Frost [64] and to examine the controversial remarks reported by others [107,108]. It is important to compare

gold with other catalytic metals under the same conditions, especially at the same dispersion, which has been often ignored in the past discussions. The selectivity and activity for methanol synthesis differ only a little among IB metals; basic metal oxides bring about methanol selectivity (Fig. 7) and the activity per unit surface area increases with a decrease in particle diameter in the case of Au [109].

Gold was reported to be very selective in the hydrogenation of olefins although less active than Pd and Pt [110,111]. Once dissociated hydrogen is supplied gold is active for hydrogenation [112]. Butadiene can be selectively transformed to butene with 100% selectivity [65–67]. A highly dispersed Au/ZrO₂ catalyst prepared from amorphous alloy gives 100% selectivity to monoalkenes from butadiene, propadiene, and propyne and exhibits preference for hydrogenation of C = O bonds over that of C = C bonds in the hydrogenation of unsaturated carbonyl compounds while the same catalytic systems prepared by impregnation exhibit much lower catalytic activity and inferior selectivity [67]. Isomerization is often depressed [2,113,114].

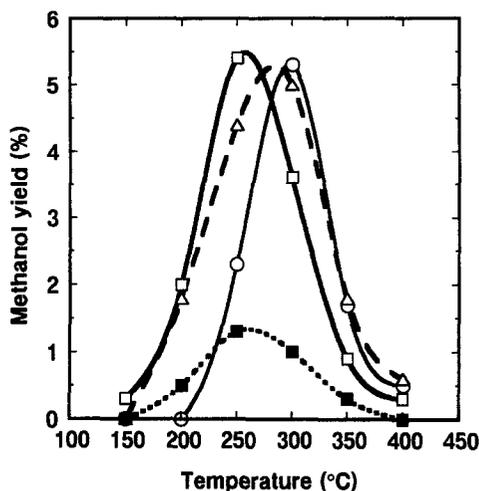


Fig. 7. Methanol yield as a function of reaction temperature in the hydrogenation of CO₂ over supported gold catalysts. ○, Au/ZnO (Au/Zn = 1:19); □, Au/α-Fe₂O₃ (Au/Fe = 1:19); △, Cu/ZnO (Cu/Zn = 1:19); ■, Au/TiO₂ (Au/Ti = 1:19). CO₂/H₂/Ar = 23:67:10, 50 atm, SV = 3000 ml/h per g-cat.

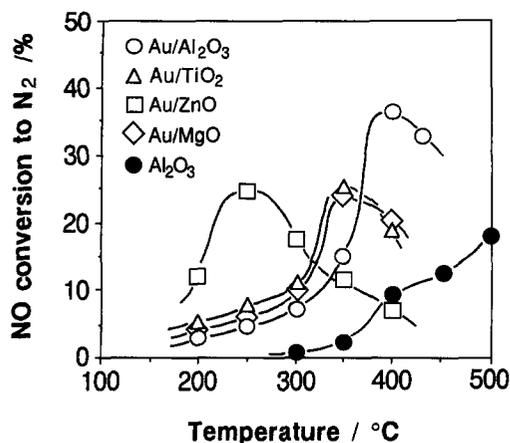


Fig. 8. Temperature dependence of NO conversion to N₂ over Al₂O₃ and gold supported on a variety of metal oxides. Au loading, 1.0 wt%; reaction gas, NO 1000 ppm + C₃H₆ 500 ppm + O₂ 5.0 vol% + H₂O 1.8 vol% + He balance; space velocity 2 × 10⁴ ml/h per g-cat.

The activity for hydrogenolysis is much less than that of Pt group metals [115]. These results indicate prospects for supported gold catalysts to be applied to controlled hydrogenation of unsaturated compounds.

6.2. Reaction of nitrogen oxides

The decomposition of N₂O takes place at 300–425°C over evaporated Au films [116] and at 830–990°C over Au filaments [117]. Since oxygen adsorption hardly takes place the reaction rate is dependent linearly on N₂O concentration alone.

The reduction of NO with CO in the absence of oxygen occurs at temperatures below 100°C over gold supported on α-Fe₂O₃ or NiFe₂O₄ yielding N₂ as a main product [118], while the product over unsupported gold is N₂O [88]. Au(I)/ZSM-5 is also reported to be active for this reaction at low temperature [119]. On the other hand, Pt-group metals require higher temperatures and yield much more N₂O. The CO + NO reaction is appreciably decelerated by the presence of O₂ but not by H₂O over Au/α-Fe₂O₃.

The reduction of NO with propylene takes place over several supported gold catalysts and is accelerated by the presence of O₂ and H₂O [68]. Fig. 8 shows that ZnO, MgO, TiO₂, and Al₂O₃ supports bring about activities from low temperature (200°C) to high temperature (500°C) and that Al₂O₃ support gives the highest conversion of NO to N₂. Over the Au/Al₂O₃ catalyst NO is oxidized to NO₂ which then reacts with C₃H₆ to form N₂. The addition of Mn₂O₃ to Au/Al₂O₃ for enhancing NO₂ formation markedly improves the conversion of NO to N₂ over a wide range of temperature [120]. This composite gold catalyst offers one of the best performances in NO conversion among the catalysts so far developed.

6.3. Reaction of halogen compounds

Gold supported on Co₃O₄ or Al₂O₃ is as active as Pt catalysts for the oxidation-decomposition of CCl₂F₂ and CH₃Cl [69,70]. It has also been reported that Au/LaF₃ is as active as Pt/LaF₃ for the synthesis of HCN through the reaction of fluorinated hydrocarbons with NH₃ [71]. The advantageous feature of supported gold catalysts over Pt catalysts for the above reactions is claimed to be their better stability.

6.4. Photocatalytic hydrogen production

In the photocatalytic production of hydrogen from the aqueous solutions of ethylene glycol [72] or ethanol [73] by TiO₂, the catalytic activity of Au is found to be about 70% of that of Pt under the same metal loading. Since the mean particle diameters of Au and Pt were 4.6 nm and 2.4 nm, respectively, the above result suggests that gold is not so inferior to Pt. In the complete photocatalytic decomposition of water [121,122], the recombination of H₂ and O₂ produced should be avoided. In this respect, gold seems to be more suitable because it is much less active in hydrogen oxidation than Pt.

6.5. Other reactions

There are two reactions for which gold is proved, or is expected to be, the most active catalytic material. In the hydrochlorination of acetylene for the manufacture of vinyl chloride monomer, it is indicated that the rate-determining step involves the addition of HCl to a surface metal-acetylene complex, whose stability is a major parameter in determining the catalytic activity and selectivity of metal chlorides. Since the standard electrode potential for the reaction of $M^{n+} + ne^- \rightarrow M$ can be correlated with the formation of both metastable acetylides and complexes with HCl, Au(III) cation which has the largest standard reduction potential, $E^\circ = 1.42$ V has been predicted to be the most active [123]. In fact gold supported on activated carbon exhibits greater activity than Hg(II) and Pd(II) chlorides [74].

For the production of hydrogen peroxide, previous experimental work mostly involved Pd-based catalysts supported on activated carbon. However, overall analysis of all the elementary steps through the Bond Order Conservation–Morse Potential Method predicts that gold is more active than Pd, Pt, and Ag [124]. It was revealed that oxygen dissociation over gold was more difficult and thus the formation of surface OOH should be enhanced and the activation energy for the reaction of $OOH + H \rightarrow H_2O_2$ is low.

7. Applications of highly dispersed gold catalysts

Gold has been commercially used for bimetallic Pd–Au catalysts supported on SiO_2 in the production of vinyl acetate from ethylene and acetic acid [125]. Notable recent advances are the reduction of NO_2 with H_2 to form NO over Au/ Al_2O_3 at around 300°C in the synthetic processes of nylon-66 [126] and the oxidation–decomposition of odors, mainly amine-

related compounds, over Au/ α - Fe_2O_3 carried on zeolite-coated honeycomb in modern Japanese toilets [127].

There are several other candidates which are technologically ready for commercial applications. These applications have been motivated by the interesting fact that supported gold catalysts are usually enhanced in their activities by moisture [90,128]:

- (1) CO_2 regeneration catalysts for sealed, unheated CO_2 lasers [40,129–131].
- (2) CO safety gas masks [132].
- (3) CO removal from air to produce high-purity N_2 and O_2 gas [90].
- (4) CO gas sensors [10].

Although the above on-going applications of gold catalysts cover only limited area in comparison with those of Pt-group metals, there are many prospects for widening its capabilities and applications in the near future.

1. Chemical industries: it is desired to develop novel chemical processes which can save energy and resources and can minimize burdens to the environment. Gold will make a significant contribution to the selective oxidation of hydrocarbons with oxygen and selective hydrogenation of unsaturated hydrocarbons.
2. Environmental protection and maintenance: in addition to indoor-air cleaning at ambient temperature gold catalysts will be effective for the protection of the global environment, for example, decomposition of halogenated hydrocarbons, reduction and decomposition of NO and N_2O .
3. Chemical sensors: semiconductor-type gas sensors have already been developed [10,133–141]. Optical gas sensors will provide a new technological advance because they are resistant to electrical noises and enable the recognition of gas molecules by using light with different wave lengths [142–144].
4. Electrochemical process: the electrochemistry of gold is also expected to find its application in fuel cells, batteries, and some

electrochemical sensors. One example is an electrode for methanol fuel cells [145].

8. Conclusion

Although the surface of gold is intrinsically inert, the catalytic nature of gold has been found to be tunable for many important reactions through the control of its particle size, the suitable selection of support materials, and the architecture of the metal-support interaction. These features promise two important opportunities for gold in the science and technology of catalysis. The markedly large structure sensitivity of activity and selectivity will offer interesting topics for fundamental research at an atomic scale. The wide range in tunability of catalytic properties from oxidation to hydrogenation presents future opportunities for industrial and environmental applications. In particular since supported gold catalysts are especially active at low temperatures, applications at ambient temperatures for environmental maintenance will be a significant contribution of gold catalysts.

References

- [1] G.C. Bond, *Gold Bull.*, 5 (1972) 11.
- [2] P.A. Sermon and G.C. Bond, *J. Chem. Soc. Faraday I*, 74 (1978) 385.
- [3] S. Galvagno and G. Parravano, *J. Catal.*, 55 (1978) 178.
- [4] I.E. Wachs, *Gold Bull.*, 16 (1983) 98.
- [5] J. Schwank, *Gold Bull.*, 16 (1983) 103.
- [6] J. Schwank, *Gold Bull.*, 18 (1985) 2.
- [7] B. Hammer and J.K. Nørskov, *Nature*, 376 (1995) 238.
- [8] M. Haruta, N. Yamada, T. Kobayashi and S. Iijima, *J. Catal.*, 115 (1989) 301.
- [9] A. Ueda and M. Haruta, *Shigen Kankyo Taisaku (Resources and Environment)*, 28 (1992) 1035.
- [10] N. Funasaki, A. Henmi, S. Ito, Y. Asano, S. Yamashita, T. Kobayashi and M. Haruta, *Sensors and Actuators B*, 13–14 (1993) 536.
- [11] H. Kita, H. Nakajima and K. Hayashi, *J. Electroanal. Chem.*, 190 (1985) 141.
- [12] L.D. Burke, D.T. Buckley and J.A. Morrissey, *Analyst*, 119 (1994) 841.
- [13] B.M.W. Trapnell, *Proc. Roy. Soc., Ser. A*218 (1953) 566.
- [14] Y. Iizuka, H. Fujiki and M. Haruta, unpublished data.
- [15] J.J. Pireaux, M. Chtaub, J.P. Delrue, P.A. Thiry, M. Liehr and R. Caudano, *Surf. Sci.*, 141 (1984) 211, 221.
- [16] T. Fukushima, S. Galvagno and G. Parravano, *J. Catal.*, 57 (1979) 177.
- [17] N.D.S. Canning, D. Outka and R.J. Madix, *Surf. Sci.*, 141 (1984) 240.
- [18] M.A. Lazaga, D.T. Wickham, D.H. Parker, G.N. Kastanas and B.E. Koel, in: S.T. Oyama and J.W. Hightower, Eds., *ACS Symposium Series 523, Catalytic Selective Oxidation*, Am. Chem. Soc., Washington, DC, 1993, pp. 90–109.
- [19] W.M.H. Sachtler and N.H. de Boer, *J. Phys. Chem.*, 64 (1960) 1579.
- [20] P.C. Richardson and D.R. Rossington, *J. Catal.*, 20 (1971) 420.
- [21] W.R. McDonald and K.E. Hayes, *J. Catal.*, 18 (1970) 115.
- [22] S. Evans, E.L. Evans, D.E. Parry, M.J. Tricker, M.J. Walters and J.M. Thomas, *Chem. Soc. Faraday Diss.*, 58 (1975) 1975.
- [23] M.E. Bartran and B.E. Koel, *Surf. Sci.*, 213 (1989) 137.
- [24] Y. Takasu, K. Yasuda, Y. Matsuda and I. Toyoshima, *Chem. Phys. Lett.*, 152 (1988) 105.
- [25] P.J. Schmitz, H.C. Kang, W.-Y. Leung and P.A. Thiel, *Surf. Sci.*, 248 (1991) 287.
- [26] P. Dumas, R.G. Tobin and P.L. Richards, *Surf. Sci.*, 171 (1986) 579.
- [27] F. Boccuzzi, S. Tsubota and M. Haruta, *J. Electron Spectros. and Rel. Phenom.*, 64/65 (1993) 241.
- [28] D.A. Outka and R.J. Madix, *J. Amer. Chem. Soc.*, 109 (1987) 1708.
- [29] L. Stobinski and R. Dus, *Surf. Sci.*, 298 (1993) 101.
- [30] D.J.C. Yates, *J. Colloid Interf. Sci.*, 29 (1969) 194.
- [31] D.A. Outka and R.J. Madix, *J. Vac. Sci. Technol.*, A3 (1985) 1680.
- [32] T. Smith, *J. Colloid Interf. Sci.*, 75 (1980) 51.
- [33] G.L. Gaines Jr., *J. Colloid Interf. Sci.*, 79 (1981) 295.
- [34] R.T. McNerney, Paper presented at 1985 Symp. Recent Adv. Air Pollution Monitoring Instrum., Raleigh, North Carolina.
- [35] D.M. Jaffey and R.J. Madix, *Surf. Sci.*, 258 (1991) 359.
- [36] *Chem. Engng. News.*, May 27, 1991, pp. 24.
- [37] C.A. Widrig, C.A. Alves and M.D. Porter, *J. Amer. Chem. Soc.*, 113 (1991) 2805.
- [38] N. Camillone III, C.E.D. Chidsey, G. Liu, T.M. Putvinski and G. Scoles, *J. Chem. Phys.*, 94 (1991) 8493.
- [39] S. Mori and Y. Shitara, *Appl. Surf. Sci.*, 78 (1994) 269.
- [40] J.A. Macken, S.K. Yagnik and M.A. Samis, *IEEEJ. Quantum Electronics*, 25 (1991) 1695.
- [41] D.M. Cox, R. Brickman, K. Creegan and A. Kaldor, *Z. Phys. D-Atoms, Molecules and Clusters*, 19 (1991) 353.
- [42] H. Huber, D. McIntosh and G.A. Ozin, *Inorg. Chem.*, 16 (1977) 975.
- [43] S. Tsubota, M. Haruta, T. Kobayashi, A. Ueda and Y. Nakahara, in: G. Poncelet et al., Eds., *Preparation of Catalysts V*, Elsevier Science B.V., 1991, pp. 695–704.
- [44] T. Kobayashi, M. Haruta, S. Tsubota and H. Sano, *Sensors and Actuators*, B1 (1990) 222.
- [45] M. Okumura, K. Tanaka, A. Ueda and M. Haruta, *Solid State Ionics*, in press.

- [46] S.D. Lin, M. Bollinger and M.A. Vannice, *Catal. Lett.*, 17 (1993) 245.
- [47] C. Sze, E. Gulari and B.G. Demczyk, *Mater. Res. Soc. Proc.*, 286 (1993) 143.
- [48] M. Haruta, A. Ueda, G.R. Bamwenda, R. Taniguchi and M. Azuma, *Proc. Int. Workshop Catal. Combustion*, Tokyo, April 18–20, 1994, pp. 2–9; G.R. Bamwenda, S. Tsubota, T. Nakamura and M. Haruta, *Catal. Lett.*, submitted for publication.
- [49] S. Tsubota, D.A.H. Cunningham, Y. Bando and M. Haruta, in: G. Poncelet et al., Eds., *Preparation of Catalysts VI*, Elsevier Science B.V., 1995, pp. 227–235.
- [50] D. Cunningham, S. Tsubota, N. Kamijo and M. Haruta, *Res. Chem. Intermed.*, 19 (1993) 1.
- [51] D.R. Schryer, B.T. Upchurch, J.D. Van Norman, K.G. Brown and J. Schryer, *J. Catal.*, 122 (1990) 193.
- [52] F. Boccuzzi, A. Chiorino, S. Tsubota and M. Haruta, *J. Phys. Chem.*, 100 (1996) 3625.
- [53] M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M.J. Genet and B. Delmon, *J. Catal.*, 144 (1993) 175.
- [54] M. Haruta, T. Kobayashi, S. Tsubota and Y. Nakahara, *Chem. Express*, 3 (1988) 159.
- [55] S. Tsubota, N. Yamada, M. Haruta, T. Kobayashi and Y. Nakahara, *Chem. Express*, 5 (1991) 349.
- [56] M. Haruta, A. Ueda, S. Tsubota and R.M. Torres Sanchez, *Catal. Today*, in press.
- [57] R.D. Waters, J.J. Weimer and J.E. Smith, *Catal. Lett.*, 30 (1995) 181.
- [58] R. Nakamura, S. Suzuki, R. Aida and H. Niiyama, *Proc. 24th Meet. Chem. Engng. Soc. Japan*, I (1991) 166.
- [59] T. Hayashi and M. Haruta, *Shokubai (Catalysts and Catalysis)*, 37 (1995) 72.
- [60] S.A. Nyarady and R.E. Sievers, *J. Amer. Chem. Soc.*, 107 (1985) 3726.
- [61] H. Sakurai, S. Tsubota and M. Haruta, *Appl. Catal. A: General*, 102 (1993) 125.
- [62] H. Sakurai and M. Haruta, *Appl. Catal. A: General*, 127 (1995) 93.
- [63] A. Baiker, M. Kilo, M. Maciejewski, S. Menzi and A. Wokaun, in: L. Guzey et al., Eds., *New Frontiers in Catalysis*, Elsevier Science B.V., 1992, pp. 1257–1266.
- [64] J.C. Frost, *Nature*, 334 (1988) 577.
- [65] D.A. Buchanan and G. Webb, *J. Chem. Soc. Faraday I*, 70 (1978) 134.
- [66] K. Ann, U. Yappushii, K. Imamura, R. Nakamura and H. Niiyama, *Proc. 57th Annual Meet. Chem. Engng. Soc. Japan*, 1992, p. 330.
- [67] M. Shibata, N. Kawata, T. Masumoto and H. Kimura, *Japan–France Seminar on Catalysis with Metal Compounds*, Tokyo, 1987, pp. 98–100.
- [68] A. Ueda and M. Haruta, *Appl. Catal. B: Environmental*, in press.
- [69] T. Aida, R. Higuchi and H. Niiyama, *Chem. Lett.*, (1990) 2247 and *Kagaku Kogaku Ronbunshu*, 17 (1991) 943.
- [70] B. Chen, C. Bai, R. Cook and J. Wright, 14th North American Meeting of the Catalysis Society, Snowbird, Utah, June 1995, T7–8.
- [71] Y. Takita, T. Imamura, Y. Mizuhara, Y. Abe and T. Ishihara, *Appl. Catal. B: Environmental*, 1 (1992) 79.
- [72] G.R. Bamwenda, S. Tsubota, T. Kobayashi and M. Haruta, *J. Photochem. Photobiol. A: Chem.*, 77 (1994) 59.
- [73] G.R. Bamwenda, S. Tsubota, T. Nakamura and M. Haruta, *J. Photochem. Photobiol. A: Chem.*, 89 (1995) 177.
- [74] B. Nkosi, M.D. Adams, N.J. Coville and G.J. Hutchings, *J. Catal.*, 128 (1991) 366,378.
- [75] M. Haruta, *Shokubai (Catalysts and Catalysis)*, 36 (1994) 310 and *Sekiyu Gakkaishi*, 37 (1994) 480.
- [76] T. Itoh, M. Demura, M. Abe and Y. Tamaura, *J. Appl. Phys.*, 69 (1991) 4913.
- [77] S. Takamatsu, M. Ishii, M. Imagawa, H. Kinbara, T. Kikuta and T. Fukushima, *Shokubai (Catalysts and Catalysis)*, 34 (1992) 126.
- [78] A. Knell, P. Barnickel, A. Baiker and A. Wokaun, *J. Catal.*, 137 (1992) 306.
- [79] S.T. Tanielyan and R.L. Augustine, *Appl. Catal. A: General*, 85 (1992) 73.
- [80] S.D. Lin, M. Bollinger and M.A. Vannice, *Catal. Lett.*, 17 (1993) 245.
- [81] C. Sze, E. Gulari and B.G. Demczyk, *Mater. Res. Soc. Proc.*, 286 (1993) 143.
- [82] G.B. Hoflund, S.D. Gardner, D.R. Schryer, B.T. Upchurch and E.J. Kielin, *Appl. Catal. B: Environ.*, 6 (1995) 117.
- [83] W. Liu and M. Flytzani-Stephanopoulos, *J. Catal.*, 153 (1995) 304, 317.
- [84] Y.-M. Kang and B.-Z. Wan, *Appl. Catal. A: General*, 128 (1995) 53.
- [85] A. Baiker, M. Maciejewski, S. Tagliaferri and P. Hug, *J. Catal.*, 151 (1995) 407.
- [86] D.A. Outka and R.J. Madix, *Surf. Sci.*, 179 (1987) 351.
- [87] N.W. Cant and P.W. Fredrickson, *J. Catal.*, 37 (1975) 531.
- [88] A.G. Dalglish and D.D. Eley, *Proc. 2nd Int. Congr. Catal.*, Paris, 1960, pp. 1615–1626.
- [89] W. Vogel, D.A.H. Cunningham and M. Haruta, *Catal. Lett.*, 40 (1996) 175.
- [90] M. Haruta, T. Takase and T. Kobayashi, in: S. Yoshida et al., Eds., *Catal. Sci. Technol. Vol. 1*, Kodansha, 1991, pp. 331–334.
- [91] Y. Iizuka, H. Fujiki, N. Yamauchi, T. Chijiwa, S. Arai, S. Tsubota and M. Haruta, *Catal. Today*, 36 (1997) 115–123.
- [92] Y. Iizuka, H. Fujiki, N. Yamauchi, T. Chijiwa, S. Arai, S. Tsubota and M. Haruta, *Proc. 69th ACS Symp. Colloid Surf. Sci.*, Salt Lake City, June 1995, p. 296.
- [93] L.V. Zavarykina, E.I. Yushkova, G.D. Kazakova and Yu.S. Mardashev, *Russian J. Phys. Chem.*, 68 (1994) 322.
- [94] C.N. Hodges and L.C. Roselaar, *J. appl. Chem. Biotechnol.*, 25 (1975) 609.
- [95] E.T. Blues, D. Bryce-Smith, I.W. Lawston and G.D. Wall, *J. Chem. Soc., Chem. Commun.*, (1974) 513.
- [96] N.W. Cant and W.K. Hall, *J. Phys. Chem.*, 75 (1971) 2914.
- [97] G. Manara and G. Parravano, *J. Catal.*, 23 (1971) 379.

- [98] G. Manara and G. Parravano, *J. Catal.*, 32 (1974) 72.
- [99] L. Han, S. Tsubota, T. Kobayashi and M. Haruta, *J. Chem. Soc., Chem. Commun.* (1995) 93.
- [100] T. Hayashi, S. Tsubota and M. Haruta, *Ind. Eng. Chem. Res.*, 34 (1995) 2298.
- [101] K. Tanaka, T. Hayashi and M. Haruta, *J. Jpn. Inst. Metals*, 60 (1996) 693.
- [102] S. Naito and M. Tanimoto, *J. Chem. Soc. Chem. Soc.* (1988) 832.
- [103] M.J. Bollinger, R.E. Sievers, D.W. Fahey and F.C. Fehsenfeld, *Anal. Chem.*, 55 (1983) 1980.
- [104] *Chem. Eng. News*, June 24, 1985, pp. 43–44.
- [105] I. Eskendirov, N.J. Coville and V.D. Sokolovskii, *Catal. Lett.*, 35 (1995) 33.
- [106] M. Shibata, N. Kawata, T. Masumoto and H. Kimura, *Chem. Lett.* (1985) 1605.
- [107] E.A. Shaw, A.P. Walker, T. Rayment and R.M. Lambert, *J. Catal.*, 134 (1992) 747.
- [108] S. Lin and M.A. Vannice, *Catal. Lett.*, 10 (1991) 47.
- [109] H. Sakurai and M. Haruta, *Catal. Today*, 29 (1996) 361.
- [110] R.S. Yolles, B.J. Wood and H. Wise, *J. Catal.*, 21 (1971) 66.
- [111] C.T.H. Stoddart and C. Kemball, *J. Colloid Sci.*, 11 (1956) 532.
- [112] B.J. Wood and H. Wise, *J. Catal.*, 5 (1966) 135.
- [113] G.C. Bond and P.A. Sermon, *Gold Bull.*, 6 (1973) 102.
- [114] G.C. Bond, P.A. Sermon, G. Webb and D.A. Buchanan, *J. Chem. Soc., Chem. Commun.*, (1973) 444.
- [115] G. Meitzner, W.J. Mykytka and J.H. Sinfelt, *J. Catal.*, 98 (1986) 513.
- [116] V.M. Stepanov, V.D. Yagodovskii and H. Agilar, *Russian J. Phys. Chem.*, 49 (1975) 1335.
- [117] C.N. Hinshelwood and C.R. Prichard, *Proc. Roy. Soc.*, 108A (1925) 211.
- [118] A. Ueda, M. Haruta, T. Kobayashi, S. Tsubota and Y. Nakahara, 59th Spring Meet. Chem. Soc. Jpn. 1A548, Tokyo, Japan (1990).
- [119] S. Qiu, R. Onishi and M. Ichikawa, *J. Phys. Chem.*, 98 (1994) 2719.
- [120] A. Ueda and M. Haruta, 1st World Congr. Environmental Catal., Pisa, May 1995, pp. 343–346.
- [121] K. Sayama and H. Arakawa, *Chem. Lett.*, (1992) 253.
- [122] K. Domen, J. Yoshimura, T. Sekine, A. Tanaka, T. Onishi, *Catal. Lett.*, 4 (1990) 339.
- [123] G.J. Hutchings, *J. Catal.*, 96 (1985) 292.
- [124] P.P. Olivera, E.M. Patrino and H. Sellers, *Surf. Sci.*, 313 (1994) 25.
- [125] *Gold Bull.*, 28(2) (1995) 33 and 26(3) (1993) 86.
- [126] Jpn. Patent, Tokai-kai-hei 8-40710 (1996) and Ger. Patent DE 4419464A1 (1995).
- [127] Matsushita Housing Products Co., Ltd., Private Communication and also see Ref. [9].
- [128] D.A.H. Cunningham, T. Kobayashi, N. Kamijo and M. Haruta, *Catal. Lett.*, 25 (1994) 257.
- [129] E. Tsuchida and H. Sato, *Jap. J. Appl. Phys.*, 29 (1990) L964.
- [130] A.K. Tripathi, N.M. Gupta, U.K. Chatterji and R.M. Iyer, *Indian J. Technol.*, 30 (1992) 107.
- [131] S.D. Gardner, G.B. Hoflund, B.T. Upchurch, D.R. Schryer, E.J. Kielin and J. Schryer, *J. Catal.*, 129 (1991) 114.
- [132] M. Haruta, *Hyomen (Surface)*, 28 (1990) 333.
- [133] J.J. McNerney and P.R. Buseck, *Science*, 178 (1972) 611.
- [134] U.S. Patent, 5,386,715.
- [135] T. Kobayashi, M. Haruta, H. Sano and M. Nakane, *Sensors and Actuators*, 13 (1988) 339.
- [136] T. Kobayashi, M. Haruta and H. Sano, *Chem. Express*, 4 (1989) 217.
- [137] T. Kobayashi, M. Haruta, S. Tsubota, H. Sano and B. Delmon, *Sensors and Actuators*, B1 (1990) 222.
- [138] D.J. Dwyer, S. Kennedy and S. Marohn, Proc. 3rd Intern. Meet. Chem. Sensors, Cleveland, September 1990, pp. 350–353.
- [139] T. Maekawa, J. Tamaki, N. Miura and N. Yamazoe, *Chem. Lett.*, (1992) 639.
- [140] M. Ando, S. Suto, T. Suzuki, T. Tsuchida, C. Nakayama, N. Miura and N. Yamazoe, *Chem. Lett.*, (1994) 335.
- [141] K. Fukui and M. Nakane, *Sensors and Actuators*, B24–25 (1995) 486.
- [142] T. Kobayashi, M. Ando and M. Haruta, *Chem. Sensors*, 9 (1993) 143.
- [143] M. Ando, T. Kobayashi and M. Haruta, *J. Chem. Soc., Faraday Trans.*, 90 (1994) 1011.
- [144] M. Ando, T. Kobayashi and M. Haruta, *Sensors and Actuators*, B24–25 (1995) 851.
- [145] P.C. Biswas, Y. Nodasaka, M. Enyo and M. Haruta, *J. Electroanal. Chem.*, 381 (1995) 167.