Advances in the catalysis of Au nanoparticles

Masatake Haruta [a,*], Masakazu Daté [b]

[a] *Research Institute for Green Technology, Institute of Advanced Industrial Science and Technology, 16-1 Onogawa, Tsukuba 305-8569, Japan*
[b] *Special Division of Green Life Technology, Institute of Advanced Industrial Science and Technology,*
1-8-31 Midorigaoka, Ikeda 563-8577, Japan

Abstract

Gold catalysts have recently been attracting rapidly growing interests due to their potential applicabilities to many reactions of both industrial and environmental importance. This article reviews the latest advances in the catalysis research on Au. For low-temperature CO oxidation mechanistic arguments are summarized, focusing on Au/TiO_2 together with the effect of preparation conditions and pretreatments. The quantum size effect is also discussed in the adsorption and reaction of CO over Au clusters smaller than 2 nm in diameter. In addition, recent developments are introduced in the epoxidation of propylene, water-gas-shift reaction, hydrogenation of unsaturated hydrocarbons, and liquid-phase selective oxidation. The role of perimeter interface between Au particles and the support is emphasized as a unique reaction site for the reactants adsorbed separately, one on Au and another on the support surfaces. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Gold has long been regarded as a poorly active catalyst. A recent theoretical calculation has explained why the smooth surface of Au is noble in the dissociative adsorption of hydrogen [1]. However, when Au is deposited as nanoparticles on metal oxides by means of co-precipitation and deposition–precipitation techniques, it exhibits surprisingly high catalytic activity for CO oxidation at a temperature as low as 200 K [2,3]. This finding has motivated many scientists and engineers to investigate the catalysis of Au in 1990s. The recent reversal of the market prices of Au (US$ 9/g) with respect to Pd (US$ 14/g) and Pt (US$ 14/g) can drive Au catalysts to commercialization with an economical advantage.

Fig. 1 shows that the annual numbers of research articles related to the catalyses of Au appreciably increased in the last decade, especially very rapidly from 1997. A citation database service, "The Web of Science", provided by Institute for Scientific Information (ISI, http://www.isinet.com/isi), was used for search through the key words of 'gold', 'catalysis', 'catalyst(s)', 'catalytic(al), 'catalytically' and conjugations of the verb 'catalyze' and 'catalyse'. For an extended search, derivatives of 'electrocatalysis', 'photocatalysis' and 'autocatalysis' were also added. The articles that contain at least one of these words in the title, abstract and key word lists are automatically counted in the numbers, which therefore include a few articles that are not really concerned with the catalysis of Au.

Since previous review articles have covered scientific work until 1999 [4–10], this paper has focused on the advances in the catalysis research of Au since then. A specific emphasis is put on the

* Corresponding author. Tel.: +81-298-61-8240;
fax:+81-298-61-8240.
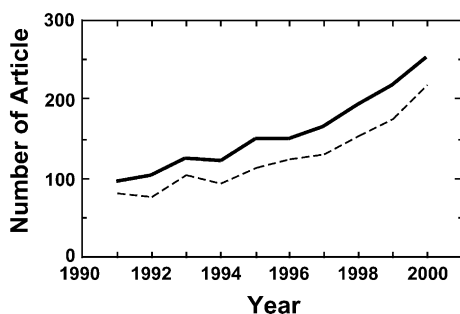*E-mail address:* m.haruta@aist.go.jp (M. Haruta).

Fig. 1. The numbers of articles concerning gold catalysts in the last decade. Dashed and solid lines denote the basic and extended search, respectively (see text).

effect of the size of Au particles on the catalytic performance.

2. CO oxidation

The oxidation of CO is a typical reaction for which Au catalysts are extraordinarily active at room temperature and much more active than the other noble metals catalysts at temperatures below 400 K. 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. One of the focuses of recent work is the mechanism for CO oxidation [7,9,10]. The following are a summary of the answers, given to the major questions, which we think are critical to the mechanism.

2.1. Active state of Au

Active catalysts always contain metallic Au particles which give CO absorption band at $2112 \, cm^{-1}$, while oxidic Au species which give CO absorption band at $2151 \, cm^{-1}$ are not responsible for steady-state high catalytic activity [11,12]. However, smooth surfaces of metallic Au do not adsorb CO at room temperature [12], indicating that CO is adsorbed only on steps, edges, and corner sites. Thus, smaller metallic Au particles are preferable [13].

Goodman and coworkers have reported an inspiring result obtained by using a model Au/TiO_2 catalyst [14]. As shown in Fig. 2, turn over frequency (TOF) for CO oxidation reaches a maximum at a diameter of
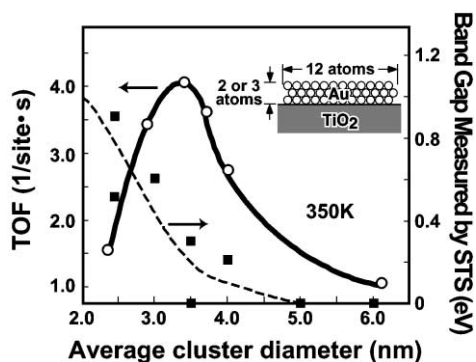

Fig. 2. Turn over frequencies and band-gap measured by STM as a function of the diameter of Au islands deposited on TiO_2 [14].

Au islands of 3.5 nm (3 atoms thick) where Au partially loses its metallic nature. They have suggested that this transition might be correlated to the high catalytic activity. Since the sample used for catalytic activity measurements was composed of the Au islands with a certain size distribution, whereas the band-gap was measured for a specific Au island by scanning tunnel spectroscopy, a more reasonable interpretation is that the ratio of the number of surface atoms of Au flat islands having metallic nature to the number of Au atoms at the periphery with the TiO_2 support reaches an optimum at a mean diameter of 3.5 nm. Since the adsorption of CO on oxidic Au sites is inhibited by moisture because of the stronger adsorption of H_2O molecule [15], activity enhancement strongly suggests that metallic Au particles are indispensable for the adsorption of CO.

2.2. Stronger contact of Au particles with the TiO_2 support

This is also indispensable for the extraordinarily high catalytic activity because the periphery sites are assumed to act as the sites for the reaction of CO adsorbed on Au and oxygen adsorbed on the support. Baiker and coworkers prepared Au/TiO_2 and Au/ZrO_2 by immobilizing Au colloids of about 2 nm size on TiO_2 and ZrO_2 and indicated that strong interfacial contact between Au and the oxides was not necessary [16,17]. Nevertheless, their observation of the activity enhancement by heating the catalyst samples in reactant stream at 423 K or calcination in Ar at 673 K

indicates the contribution of the strong contact. Later, they reported that Au/TiO_2 interface was important for oxygen activation [18].

Our experiments, using a mechanical mixture of Au colloids of about 5 nm with TiO_2 powder, clearly showed that higher calcination temperature gives higher catalytic activity, although Au particles grew to larger particles [19]. While larger number of steps, edges, corners in smaller Au particles increases the catalytic activity for CO oxidation, contact with the support contributes to an additional increase in activity at least by one order of magnitude [20]. An atomic-level model for oxygen activation at the periphery by the redox cycle between Au^{3+} (more likely Au^+) and Au^0 is proposed by Bond and Thompson [9].

2.3. Oxygen activation

No direct experimental evidence has yet been presented whether oxygen molecule is dissociatively or non-dissociatively adsorbed and on which site of supported Au catalysts it is adsorbed. However, the number of articles which indicate the adsorption in a molecular form on the metal oxide supports is increasing [7,20–24]. Until now, the most convincing evidences for molecularly adsorbed oxygen have been obtained by a temporal analysis of products (TAP) study of O_2 adsorption [22,23] and by $^{18}O_2$ isotope experiments [21–23].

The O_2^- species was detected by means of ESR when oxygen gas was introduced at room temperature after evacuating Au/TiO_2 at 673 K [21] or when $CO + O_2$ mixture was introduced to Au/TiO_2 [24]. There still remains an important argument, whether the dissociation of molecularly adsorbed oxygen takes place before reacting with CO adsorbed on the Au surfaces or the dissociation takes place through reaction. In the latter case, the formation of carbonate intermediate can be excluded because no ^{18}O scrambling to produce $C^{18}O_2$ takes place ($C^{16}O + {}^{18}O_2{}^- + e^- \rightarrow C^{18}O_2 + {}^{16}O^{2-}$).

2.4. Reaction pathways

We have presented a comprehensive reaction mechanism which can explain the whole catalytic behavior of Au/TiO_2 catalysts over a wide range of temperature from 90 to 400 K [25]. The Arrhenius plots in
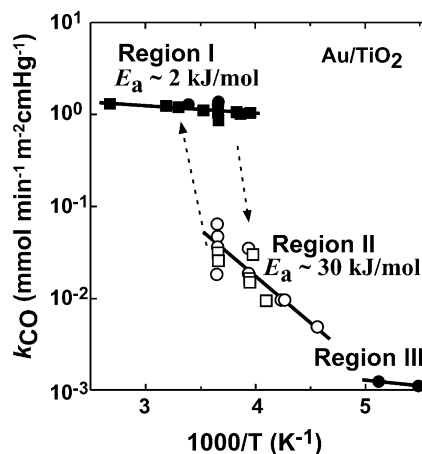
Fig. 3. Arrhenius plots for CO oxidation over Au/TiO_2 catalyst.

Fig. 3 shows that there are three temperature regions where different kinetics are operating with markedly different rates and apparent activation energies. The probable pathways for CO oxidation are schematically shown in Scheme 1.

At temperatures below 200 K, the TiO_2 surfaces and its perimeter interfaces around Au particles are covered with carbonate species. Reaction of CO with O_2 takes place only on the surfaces of Au, more

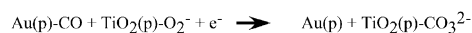Reaction at the Au Surfaces
Below 200 K

$$Au(s)\text{-}CO + Au^{\delta+}(s)\text{-}O_2{}^{\delta-} \rightarrow CO_2(g) + Au(s) + Au^{\delta+}(s)\text{-}O^{\delta-}$$

$$Au(s)\text{-}CO + Au^{\delta+}(s)\text{-}O^{\delta-} \rightarrow CO_2(g) + 2Au(s)$$

$$Au(p)\text{-}CO + Au^{\delta+}(p)\text{-}O_2{}^{\delta-} \rightarrow CO_2(g) + Au(p) + Au^{\delta+}(p)\text{-}O^{\delta-}$$

$$Au(p)\text{-}CO + Au^{\delta+}(p)\text{-}O^{\delta-} \rightarrow CO_2(g) + 2Au(p)$$

Reaction at the Perimeter Interfaces
Above 300 K

$$Au(p)\text{-}CO + TiO_2(p)\text{-}O_2{}^- \rightarrow CO_2(g) + TiO_2(p) + e^- + Au^{\delta+}(p)\text{-}O^{\delta-}$$

$$Au(p)\text{-}CO + Au^{\delta+}(p)\text{-}O^{\delta-} \rightarrow CO_2(g) + 2Au(p)$$

Below 300 K: accompanied by

$$Au(p)\text{-}CO + TiO_2(p)\text{-}O_2{}^- + e^- \rightarrow Au(p) + TiO_2(p)\text{-}CO_3{}^{2-}$$

(s): step, (p): perimeter, (g): gas phase

Scheme 1. Reaction pathways for CO oxidation over Au/TiO_2 catalyst.

specifically, on the step, edge, and corner sites with almost 0 kJ/mol for apparent activation energy. This means when Au particles are small enough the catalytic activity can be detected at any temperature. Actually unsupported Au powder (30 nm in diameter) exhibits measurable activity for CO oxidation at 200 K with apparent activation energy of nearly zero [20]. At temperatures above 300 K, reaction takes place at the perimeter interfaces between CO adsorbed on the surfaces of Au particles and molecular oxygen adsorbed at the support surface. This reaction also gives nearly zero apparent activation energy but proceeds much faster by more than one order of magnitude than the reaction over the Au surfaces. At the intermediate temperature from 200 to 300 K, the reaction proceeds at the perimeter interface which is partly covered with carbonate species. The coverage of the species may change depending on temperature, thus giving rise to apparent activation energy around 30 kJ/mol.

In addition to the above arguments, a few other interesting features of Au/TiO$_2$ catalysts are reported by using model catalysts [10,26,27] and by high resolution transmission electron microscopy [10,28–30]. Fig. 4 shows a typical epitaxy structure at the Au and the support contact [29]. More Au particles are seen at the valley between the TiO$_2$ particles when calcined at higher temperatures.

The adsorption of CO on Au surfaces is one of the important steps in CO oxidation. Boccuzzi et al. have found that an Au/TiO$_2$ catalyst prepared by deposition–precipitation contains three different Au sites for CO adsorption depending on the pretreatment conditions [15]. CO adsorbed linearly on metallic Au sites (2110–2120 cm^{-1}) after normal calcination in air, CO adsorbed on oxidic Au species (2176 cm^{-1}) which appear only after being highly dehydrated and oxidized, CO adsorbed linearly and bridge-bonded on small Au clusters (2050–1900 cm^{-1}) perturbed by the negative charge produced in support reduction by H$_2$. An adsorption study of CO and O$_2$ over Au/TiO$_2$ by using fixed bed flow reactor equipped with a mass spectroscopy has shown that CO and O$_2$ adsorption takes place instantaneously and that CO$_2$ formation increases until the oxygen adsorption on the reduced sites of perimeter reaches saturation [31]. Moreover, moisture also enhances the oxidation of CO over Au/TiO$_2$. The catalytic activity is much lower under the dry condition (0.1 ppm H$_2$O) than under the
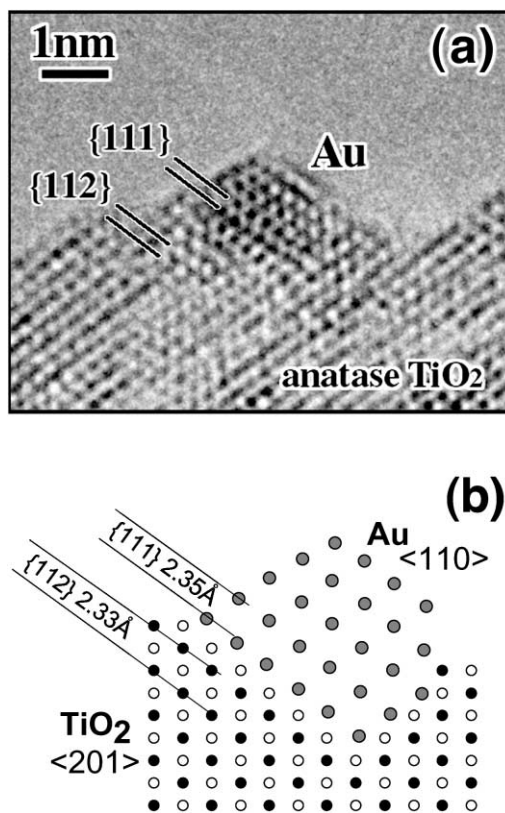

Fig. 4. (a) Transmission electron micrograph for Au/TiO$_2$ contact interface and (b) its schematic diagram.

ordinary experimental condition (about 3 ppm H$_2$O) [32].

The fundamental aspects of Au catalysis have also been studied by using single crystal of Au and model catalysts. The adsorption of CO on Au(1 1 1) was investigated by means of surface X-ray diffraction in a wide range of pressure from ultrahigh vacuum to 2 bar, showing that modification of surface structure occurs at pressures above 1 mbar of CO [33]. As a result of study of the size-selected Au anion clusters, appreciable size dependency of CO adsorption was observed: the highest reactivity to CO was observed for the anion clusters of 11 atoms [34]. As shown in Fig. 5, it was found that 8 and 11 are the smallest and the second smallest to exhibit the catalytic activity over the MgO support. The higher activity of Au clusters on defect-rich MgO than on defect-poor MgO was observed and ab initio simulations indicate that partial
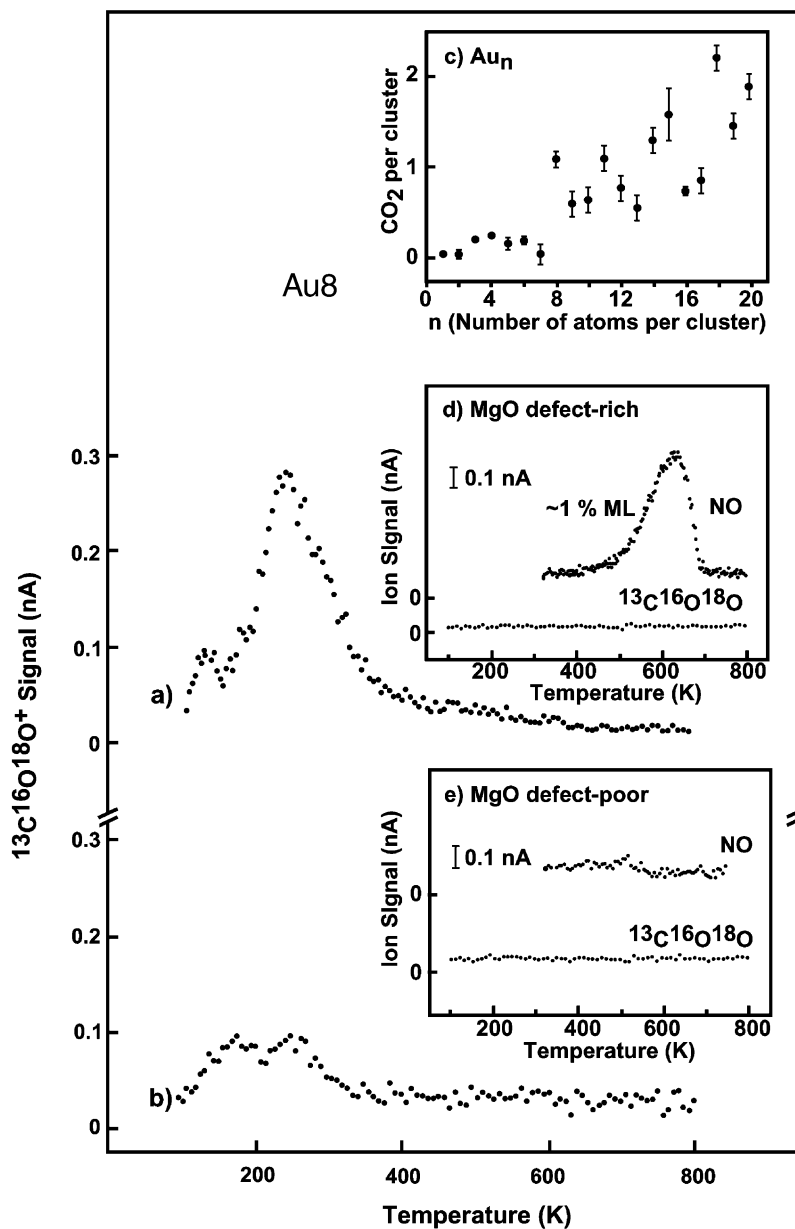
Fig. 5. Catalytic activities of Au clusters supported on MgO for CO oxidation as a function of the number of Au atoms [36].

electron transfer from the surface of the Au clusters and oxygen-vacancy defects in the support play an essential role for the genesis of catalytic activity [35,36]. An attempt to add Au atoms on Pt(3 3 5) to change CO adsorption properties may be one of the valuable approaches for a new CO oxidation catalyst [37].

Gold supported on Fe_2O_3 appears to be advantageous in commercialization over Au/TiO_2 in the lower cost and higher availability of Fe_2O_3 and in catalytic performance not only for CO oxidation but also for other reactions such as oxidative decomposition of amine compounds. There are still a few reports that

oxidic Au species act as active sites [38,39]. Although this conclusion is drawn from a relation between the amount of Au^+ in fresh catalysts and catalytic activity, the sample after reaction is speculated to be composed of increased number of small metallic Au particles and of decreased amount of oxidic Au species. The involvement of lattice oxygen of Fe_2O_3 in CO oxidation is proposed [40,41], however, because of the low reactivity and mobility of lattice oxygen at low temperatures it is more likely that oxygen adsorbed at the periphery is the active species. Recently, a few reports emphasize the importance of structural transformation of the Fe_2O_3 support [42,43].

The above Au/Fe_2O_3 catalysts were prepared by co-precipitation, whereas liquid-phase grafting by using Au-phosphine complex can also give active catalysts [44,45]. Although long-term stability of Au/Fe_2O_3 should be checked in detail, a good performance of Au/Fe_2O_3 is reported for selective CO oxidation in H_2-rich gas [46], which is now an important subject related to polymer electrolyte fuel cells.

Some papers deal with the effect of preparation and pretreatment conditions [47–53]. Unfortunately, the conclusions are not always generalized for creating highly dispersed and active Au catalysts, because the comparisons were made only among the catalyst samples which the authors made. Improvement of the impregnation method was tried by high-temperature reduction (HTR), calcination (C), and low-temperature reduction (LTR) [47]. HTR is necessary to remove chloride, while C is necessary to oxidize the catalyst surface. LTR may remove oxygen adsorbed on the Au surfaces and probably to moisten the catalyst sample, which increases the catalytic activity for CO oxidation [32]. However, the activities of thus prepared catalysts did not exceed those by deposition–precipitation.

Deposition–precipitation (DP) using urea [48,49] may not also be advantageous over that using NaOH, because NH_4^+ often causes the formation of larger Au particles. Both in DP and in co-precipitation, metal hydroxide precursors should be precipitated in a short period to have homogeneous size distribution. Therefore, in DP, the pH of aqueous solution of $HAuCl_4$ should be fixed at a point from 6 to 10 and then the support materials should be put into this solution instantaneously, whereas in co-precipitation, the aqueous mixture of $HAuCl_4$ and the metal nitrate should be added to the aqueous solution, containing an excess of Na_2CO_3 instantaneously, not by drop-wise manner [50].

One of the promising fields of application of Au catalysts is CO_2 lasers. It has long been known that coating of the inside-walls of the glass of laser discharge tube with Au resulted in the substantial improvement of the performance of sealed-off direct current excited CO_2 lasers [54]. The performance of radio-frequency excited CO_2 lasers can also be enhanced by a joint action of the Au coating of electrodes and the addition of CO at a high concentration (4–8 vol%) [55,56]. The role of CO is explained by the adsorption on the Au surfaces to prevent them from being deactivated by oxygen species. This phenomenon is consistent with the results obtained at 90 K for the reactivities of CO and oxygen preadsorbed; the latter is more stably adsorbed and less reactive to form CO_2 [12].

3. Epoxidation of propylene

Since Hayashi found that Au supported on TiO_2 (Degussa, p-25) could catalyze the epoxidation of propylene in the gas phase containing O_2 and H_2 [57], the catalytic properties of Au/TiO_2 and related systems have attracted chemical industries [58] as well as academia. Propylene oxide (PO) is one of the important bulk chemicals, which is used for producing polyurethane and polyols. It is produced in the world at 3.5 million tonnes per year, providing a market of US$ 7 billion per year. Current industrial processes need two-staged chemical reactions using either Cl_2 or organic peroxides yielding byproducts stoichiometrically. Au catalysts, which produce PO in one stage without byproducts other than H_2O, are expected to replace these processes.

There are four important factors for Au catalysts in the direct epoxidation of propylene. The first one is catalyst preparation methods. As shown in Fig. 6, impregnation method did not result in selective oxidation but complete oxidation to H_2O and CO_2, whereas DP method led to epoxidation with selectivities above 90% [59]. A major difference in the fine structure of the Au/TiO_2 catalysts is that in the case of impregnation, a large (several tens nm in diameter) spherical Au particle is simply mixed with smaller TiO_2 particles, while in the case of DP, small hemispherical Au particles are strongly contacted with a TiO_2 particle at
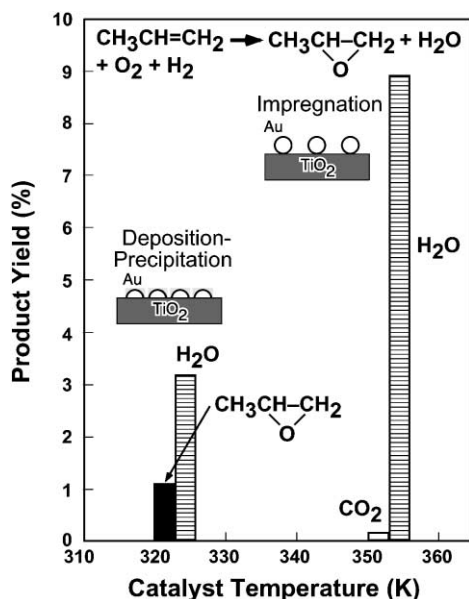
Fig. 6. Epoxidation of propylene over Au/TiO$_2$ prepared by different methods.

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 second one is the appropriate selection of the support materials. Among single metal oxides, only TiO$_2$ makes Au selective for the reaction. Furthermore, the crystalline structure of TiO$_2$ should be anatase but not rutile and amorphous [59]. Au supported on anatase is selective only at temperatures below 373 K, which is not sufficiently higher than the boiling point of PO (307 K) so that the conversion of propylene remains small. Therefore, a variety of titanium silicates, as well as Ti deposited on SiO$_2$, have been tested as a support for Au particles [58–67]. When these Ti/SiO$_2$ support materials are used, Au is selective to epoxidation up to 473 K, yielding improved conversion nearly to 5% [58,62,67]. A reaction pathway has been proposed that H$_2$O$_2$ is formed on the Au surfaces and then transformed into OOH on Ti^{4+} tetrahedrally coordinated in SiO$_2$ matrices to react there with propylene [62,66,67]. Among titanosilicates such as TS-1, Ti-β zeolite, Ti-MCM41, Ti-MCM48, having different sizes and structures of pores, Ti-MCM48 is proved to give the best catalytic

performance [67]. The atomic ratio of Ti/Si should be within 1/100–3/100 to keep Ti cations isolated from each other in the matrix. When Ti/Si exceeds 3/100, TiO$_2$ species are assembled to yield CO$_2$ at temperatures above 373 K. This upper limit on Ti/Si ratio is also valid to Ti deposited on SiO$_2$. We have also tested SiO$_2$ supports with a variety of specific surface area from 60 m^2/g (non-porous) [63] to 800 m^2/g. It appears that there is an optimum pore size, its distribution, and specific surface area.

The third one is the size of Au particles. When the mean diameter of Au particles is smaller than 2 nm, propylene is hydrogenated to form propane [57]. This phenomenon has also been confirmed by a group other than ours [66].

The fourth one is the additives. When titanium silicates are used as a support and Au is deposited by DP, complete washing to remove Na and Cl causes the propyonaldehyde formation instead of PO, while simple filtration of the Au(OH)$_3$ precursor precipitated on titanosilicates without further washing gives PO selectively [60]. This result strongly indicates that alkaline and/or chloride may play an important role in the selective epoxidation. It has been claimed that many alkaline and alkaline earth chlorides work as a good promoter [58,62]. However, the optimum amount and sites and the mechanistic role have not yet been understood.

For commercialization of the direct gas-phase epoxidation of propylene, the gradual deactivation of Au catalysts in an hourly basis is one of the problems to be solved. The reasons are partly clarified to be the accumulation of acidic and origomerized species on the catalyst surface [66,67]. Although there is no appreciable growth in the size of Au particles, the initial activity cannot be fully restored even by calcination in air at 573 K to burn off the hydrocarbon residues.

The kinetic study has also been done by Delgass and coworkers [65]. They also reported that Au(OH)$_3$ deposited on TS-1 by DP after drying can selectively give PO with conversion of propylene of about 25% by gradually raising the catalyst temperature in a stream of reactant mixture of propylene, O$_2$, and H$_2$ [68]. Although the insufficient reproducibility may be speculated, this conversion is surprisingly high, because 10% conversion at a space velocity of 7000 h^{-1} provides sufficient commercial productivity.

Fundamental research has also been initiated by Goodman's group, using Au(1 1 1) and Au(1 0 0) for the adsorption of propylene [69]. Oxygen adsorbed on these smooth surfaces was not selective to form propylene oxide. Further work on the steps, edges, corners of metallic Au nanoparticles and on Au clusters is needed.

4. Water-gas-shift reaction

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 900 K 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 CO_2 over supported Au catalysts, it was found that Au/TiO_2 was selective to the formation of CO, namely, reverse water-gas-shift reaction at a temperature as low as 473 K [70]. Later, Au/TiO_2 was confirmed to be active for water-gas-shift reaction [71]. Andreeva and her coworkers were the first to apply Au catalysts to water-gas-shift reaction [72] and reported that Au/Fe_2O_3 and Au/ZrO_2 were the most active. Recently, they reported that well-crystallized supports led to higher catalytic activity [73]. Until now, the reasons are unknown why only TiO_2 and ZrO_2 (Group IV metal oxides), and Fe_2O_3 are effective and why the crystallinity of these metal oxides appreciably affect the catalytic activity.

Although the stability may not be good, Au/NaY is reported to be active for water-gas-shift reaction at 373 K [74]. The redox cycle of Au^+ and Au^0 is assumed to operate for CO activation, while NaY support for H_2O activation.

5. Hydrogenation of unsaturated hydrocarbon

In general, the hydrogenation of hydrocarbons is structure insensitive reaction over most of metal catalysts [75]. Over supported Au catalysts it is also the case: among Al_2O_3, SiO_2, TiO_2 supports, no appre-
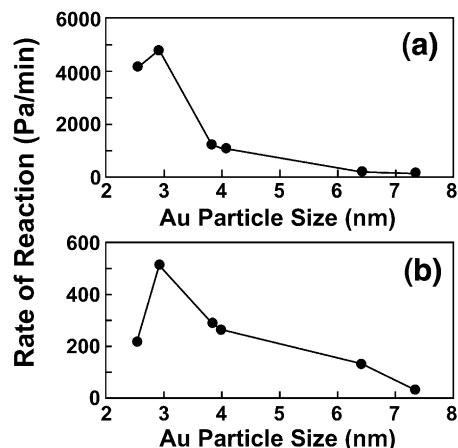

Fig. 7. Dependence of catalytic activity of Au/Al_2O_3 catalyst for (a) CO oxidation and (b) acetylene hydrogenation on the diameter of Au particles [77].

ciable difference is observed and the effect of the size of Au particles on the TOF is not obvious in butadiene hydrogenation [76].

A characteristic feature of Au catalysts is that partial hydrogenation takes place very selectively: butadiene to butenes, acetylene to ethylene [76,77]. In the hydrogenation of α, β unsaturated aldehyde, selectivity to the hydrogenation of C=O against that of C=C has been recently reported to reach 40–50% when Au particles are larger than 2 nm in diameter [78,79]. In both cases of acetylene hydrogenation over Au/Al_2O_3 (Fig. 7) and acrolein hydrogenation over Au/TiO_2 and Au/ZrO_2, the catalytic activity per unit weight increases with a decrease in the size of Au particles down to 2 nm, indicating metallic nature of Au is important for hydrogenation.

6. Liquid-phase reactions

Prati and Rossi found that Au supported on activated carbon is more active and selective than other noble catalysts for the oxidation in a MeOH–H_2O (6:4) solvent of glycols to α-hydroxy acids, which are used for cosmetics and food industries [80]. Not only activated carbon but also γ-Al_2O_3 and TiO_2 make Au active and selective [80,81]. An interesting feature is that over activated carbon support maximum activity is observed when the mean diameter of Au
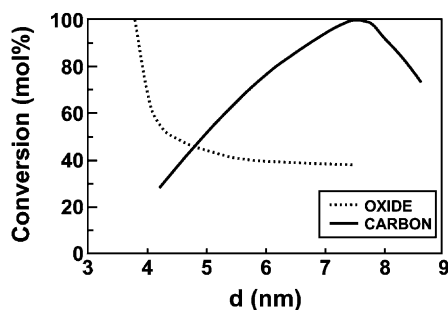
Fig. 8. Dependence of catalytic activity of Au/Al$_2$O$_3$ and Au/C catalysts for the oxidation of glycols on the diameter of Au particles [80].

particles is 7–8 nm, whereas the smaller Au particles give the higher activity over γ-Al$_2$O$_3$ and TiO$_2$ support (Fig. 8). This can be explained as follows: smaller Au particles can be easily fixed on the internal surfaces of carbon, consequently being less accessible to reagents in the liquid-phase than larger Au particles located on the external surface. It should also be noted that Au sols stabilized with polyvinylpirrolidone, and that tetrakis(hydroxymethyl) phosphonium chloride can give uniformly dispersed Au even on activated carbon by simply dipping the support materials, giving smaller mean diameter of Au in this order.

Unsupported Au nanoparticles also present great potentials as unique catalysts in liquid-phase reactions. One example has been recently reported: *N*-methylimidazole-functionalized Au particles exhibit a good catalytic activity for cleavage of a carboxylic acid ester about 30 times as high as a reference monomeric catalyst without Au particles [82].

7. Other reactions

It is interesting to know that the catalytic nature of Au itself is also applicable to NO$_x$ gas sensors [83] and to etching of Si by CF$_4$/O$_2$ plasma [84]. The surfaces of Au are more active in H$_2$O$_2$ decomposition than those of α-Al$_2$O$_3$, TiO$_2$ and SiO$_2$ [85]. This activity order is explained by the large OH–Au chemisorption bond of 155 kJ/mol with the OH radical becoming an OH$^-$ anion. Nanocrystal Au cores encapsulated with thiolate monolayer are demonstrated to be both electrochemically accessible and catalytically active for

CO oxidation upon anodic activation in the aqueous solution of KOH [86].

8. Conclusions

New knowledge extracted from recent publications on Au catalysts may be summarized as follows.

1. Extraordinarily high catalytic activity of supported Au catalysts for CO oxidation at room temperature arises from the reaction of CO adsorbed on the step, edge, and corner sites of metallic Au particles with oxygen molecules adsorbed at the perimeter sites on the support surfaces. It is unlikely that oxidic Au species and non-metallic small Au clusters are responsible for the extraordinarily high catalytic activity, although they are active to a certain extent.
2. Although catalytic chemistry of Au clusters which are no more metallic in nature may not directly lead to practically active catalysts, it can give an atomic-level understanding for the activation of oxygen at the periphery of Au particles in contact with the support.
3. It is proposed that epoxidation of propylene proceeds through the formation of H$_2$O$_2$ on the surfaces of Au particles, its capture as OOH at Ti^{4+} in tetrahedrally coordinated in SiO$_2$ matrices, and the reaction of OOH with propylene adsorbed on the support surfaces. These pathways again prefer long distance of perimeter around Au particles.
4. Supported Au catalysts are applicable to the hydrogen production through low-temperature water-gas-shift reaction and selective CO oxidation in H$_2$-rich streams, to the selective partial hydrogenation of butadiene, acetylene and unsaturated aldehyde, and to the liquid-phase selective oxidation of glycols.

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