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Gold Nanoparticle Catalysts

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# Chance and Necessity: My Encounter with Gold Catalysts

*Masatake Haruta**

gold catalysis · heterogeneous catalysis · nanoparticles

## *Catalytic Hydrogen Combustion and Balandin's Volcano Relationship*

I am often asked why I have chosen gold for my catalysis research. My answer is simple: because I was a stranger to the field of catalysis and had no preconceptions about catalytic elements.

I started my professional career at Osaka National Research Institute after receiving a PhD from Kyoto University in 1976 for research on fluorine electrochemistry.[1] I joined a hydrogen energy research project funded by the Ministry of International Trade and Industry, Japan, and was engaged in the development of space heaters and cooking ovens fueled by hydrogen.[2] Since I thought that national research institutes should focus on long-term innovative R&D programs and should not indulge in short-term technology improvements, I decided to work on base metal oxides which could replace noble metal catalysts such as palladium and platinum for initiating hydrogen combustion (oxidation) at room temperature. A wide variety of base metal oxides can be prepared by different methods under different conditions. Among them $MnO_2$, $Co_3O_4$, NiO, and $Ag_2O$ were found to be the most active for hydrogen oxidation. We then extended the catalyst survey to binary and ternary metal oxide systems of silver. My hypothesis was quite straightforward and was inspired by the volcano relationships reported by Balandin which were based on the Sabatier principle (Paul Sabatier, Nobel Laureate in Chemistry, 1912).[3]

Figure 1 shows the catalytic activity of a series of metal oxides expressed by the temperature for 50% conversion ($T_{1/2}$) of 1.0 vol% hydrogen in air at an hourly space velocity of 20000 $h^{-1}$ mL (g cat.)$^{-1}$ as a function of the enthalpy of metal oxide formation per gram-atom of oxygen, which corresponds to the metal–oxygen bond strength.[4,5] The lower the $T_{1/2}$, the higher the catalytic activity. This figure correlates kinetic with thermodynamic properties. For base metal oxides located at the right side of the volcano, catalytic activity decreases with an increase in the metal–oxygen bond strength. This is because the rate of oxygen donation from metal oxides becomes slower. In contrast, for $Ag_2O$ and Au located at the left side, because the metal–oxygen bond strength is very weak, oxygen uptake from the gas phase is relatively slow to limit the rate of oxidation. This type of volcano relation had already been reported for many reactions.[6–8] What I did was to prepare mixed oxides of metals at the left side (Ag and Au) with those at the right side.

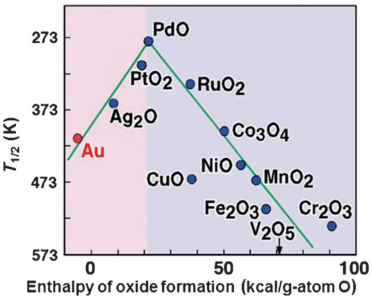

***Figure 1.*** Volcano plot correlating catalytic activity for $H_2$ oxidation (expressed by temperature for 50% conversion) and the strength of the metal–oxygen bond.

## *A Surprise: CO Oxidation at 203 K*

The best method for preparing well-mixed metal oxides is in principle coprecipitation. Mixed oxides of silver such as Ag-Mn and Ag-Mn-Co oxides were more active than any other single-base-metal oxides and were only a little less active than palladium and platinum catalysts in hydrogen oxidation. At the Third International Symposium on Scientific Bases for the Preparation of Heterogeneous Catalysts held at Louvain-la-Neuve in Belgium in September 1982, I reported experimental results concerning silver-based mixed oxides. Clyde S. Brooks, who was a technical consultant in the USA, asked me, "Have you tried gold?" I answered "No, because gold is more expensive than platinum." He was not satisfied with my answer. "If your hypothesis is correct, you can create more active catalysts by using gold. Finding new scientific principles is more important than economy in

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[*] Prof. M. Haruta
Research Center for Gold Chemistry
Department of Applied Chemistry
Graduate School of Urban Environmental Sciences
Tokyo Metropolitan University
1-1 Minami-osawa, Hachioji, Tokyo 192-0379 (Japan)
E-mail: haruta-masatake@tmu.ac.jp
Prof. M. Haruta
Gold Catalysis Research Center
Dalian Institute of Chemical Physics
457 Zhongshan Road, Dalian 116023 (P. R. China)

research and development." After a one-year stay at Professor Delmon's laboratory in Belgium and just after attending the symposium, I went back to Osaka, where I prepared mixed oxides of gold by coprecipitation. That December I received a wonderful Christmas present. Some catalysts were active at room temperature for hydrogen oxidation and surprised me when I conducted CO oxidation. Carbon monoxide disappeared from the reactant gas even at 203 K and $CO_2$ was produced.[9] It took a year and a half for my students and me to confirm our experiments on catalyst preparation and catalytic activity measurements and to reproduce our results.

## Professor Iijima Found Gold Nanoparticles

At that point the catalytically active state of gold was not known. No new X-ray diffraction peaks were observed that could be ascribed to the mixed oxides of gold, and peaks assigned to metallic gold were not evident. X-ray photoelectron spectroscopy showed peaks with a small chemical shift of about 0.4 eV toward positive values, which could be ascribed to a mixture of metallic gold particles and tiny gold clusters and atoms. On one evening in 1984 I happened to watch the evening news on TV. There was a report on Professor Sumio Iijima of Meijo University who had used a transmission electron microscope and observed ultrafine particles of gold moving around on silicon surfaces like amoeba. I decided to ask him to observe my gold catalyst samples. He was so kind to analyze them within a few days and informed me by telephone that my samples were composed of ultrafine particles of gold as shown in Figure 2.[10] I was quick to drive to Nagoya by car and received ten pictures of different sites for each sample. In the most active catalyst sample we observed 3146 particles and measured them to obtain mean diameters of gold particles of 4.5 nm with a standard deviation of 1.6 nm. Finally, we could confirm the homogeneous dispersion of gold particles and narrow distribution of particle diameters.

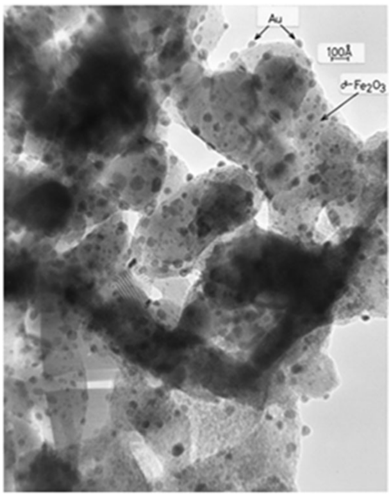

***Figure 2.*** TEM image obtained by Professor Iijima for a sample of an Au-Fe (1:19) coprecipitate calcined in air at 673 K.

## Which State of Gold Is Catalytically Active?

Following my proposal that CO oxidation takes place at the perimeter interfaces between gold nanoparticles (NPs) and the support metal oxides,[10] many other hypotheses have been presented in which different species and structures of gold are claimed to be the catalytically active sites. They are compared in Figure 3[11] in terms of turnover frequencies (TOFs, rate per exposed metal atom at the surface) at room temperature as a function of gold particle diameter or height. It should be noted that the two extremes, atomically dissociated gold cations and unsupported metallic gold in the shape of a sponge or a tube are less active by one or two orders of magnitude than supported nanostructured gold, such as clusters, thin films, and NPs. Obviously, there is an optimum size range from 0.5 to 5 nm for gold to exhibit a TOF of around 1 $s^{-1}$.

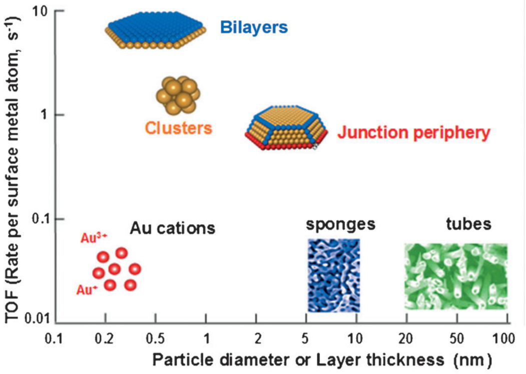

***Figure 3.*** Turnover frequency of CO oxidation at room temperature for various states of gold.

Unsupported gold sponges[12,13] show moderate catalytic activity at room temperature owing to the promoting action of $Ag_2O$ contaminants.[14] Polymer-embedded microtubes are active, but only in the presence of aqueous alkali solution.[15] Gold cations[16] are not inactive but moderately active, exhibiting higher activity on basic metal oxide supports than on neutral metal oxides.

As predicted by Kubo almost fifty years ago, small metal clusters behave differently from metal particles in the bulk.[17] This concept has been experimentally confirmed by the electronic structures of metal clusters[18] and their catalytic activity for CO oxidation. On a single-crystal MgO support, at least eight atoms of gold are necessary,[19] while on the hydroxide supports of alkaline earth metals, such as Be and Mg,[20] and La[21] 13-atom clusters are extremely active at temperatures as low as 200 K. The technical requirements are that the supported catalysts should be calcined at 553 K, and the metal loading and the diameter of gold particles should be higher than 10 wt% and smaller than 1 nm, respectively.

The thickness of a gold bilayer was proposed by Goodman and Chen using surface science models to be the critical thickness for catalysis.[22] The theoretician Pacchioni and his co-workers suggested that the gold layer can be influenced by a molybdenum substrate through a thin layer of $TiO_2$[23] and therefore Goodman's model catalysts might not be appropriate. They studied the structural and electronic properties of gold atoms and nanowires deposited at various coverages on $TiO_x$/Mo(112) thin films.

On the other hand, Au-Fe coprecipitates dried at 393 K, which contain a relatively high fraction of bilayers, exhibit higher catalytic activity at room temperature than the coprecipitates calcined at 573 K.[24] Most practical gold catalysts are prepared by calcination in air at 573 K or above in order to guarantee the stability. We have recently confirmed that one of the gold catalysts I had prepared 27 years ago still retain the initial high catalytic activity. As far as practically stable catalysts are concerned, extensive direct experimental evidence shows that gold NPs are catalytically active gold species and the perimeter interfaces act as reaction sites for CO adsorbed on the gold NPs and molecular oxygen adsorbed on the base metal oxide supports. In fact, the reaction rate for CO oxidation was found to be proportional to the length of the perimeter interface.[25]

Although the original hypothesis by Goodman and Chen does not include the contribution from the support material, it seems to be more probable that gold bilayers combined with periphery sites could provide the most gold-atom-efficient catalysts. This idea was formulated in discussions at the conference "152nd Faraday Discussions: Gold" held at Cardiff University in 2011.[11]

## *Selective Oxidation with Molecular Oxygen: Seeking Simpler Reactions*

Our gold catalysts found commercial application in Japan in 1992 for eliminating odors in restrooms. Our next target was to demonstrate their practical applicability in the chemical industry. I decided to study the selective oxidation of hydrocarbons with molecular oxygen. There are three ways to activate oxygen molecules (Figure 4). The electrochemical reaction takes place without difficulty because the dissociation energy of dioxygen is negative and very large. Reductive activation of $O_2$ with hydrogen or CO can also proceed smoothly because the dissociation energy is nearly zero. In contrast, oxygen dissociation without reducing agents requires a tremendous amount of energy, about 118 kcal mol$^{-1}$. Under the corresponding thermal conditions, it is difficult to control the reactivity of the dissociated oxygen atoms and the combustion of hydrocarbons occurs preferentially. This is why selective oxidation with molecular oxygen alone is so difficult. I felt that this is one of the most exciting topics in gold catalysis research and chose propylene as a major substrate.

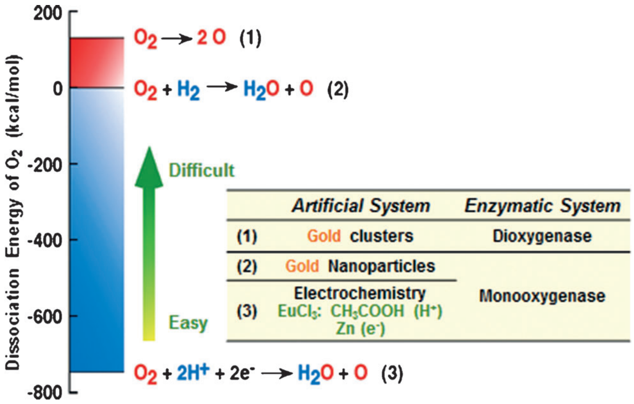

*Figure 4.* Dissociation energies of dioxygen by three different routes.

Even after four years of research, all of our experiments resulted in the combustion of propylene and our motivation decreased steadily. On a cold winter day, my research group discussed whether we should continue propylene epoxidation. No one had a burning passion to continue but I could not agree to abandon this topic of research. I proposed to add hydrogen to the reactant gases not because of the reductive activation of oxygen molecule, but based on a simple traditional idea. Zenzai (thick bean-meal soup) is a popular dessert in winter in Japan. The most effective means of intensifying the sweetness of the soup is the addition of a small amount of salt. This idea motivated Toshio Hayashi to study propylene epoxidation with $O_2$ and $H_2$.[26] We could finally demonstrate sufficiently good catalytic performance for commercial applications (conversion 8%, selectivity above 90%, hydrogen utilization efficiency above 30%);[27] however, safety against explosion is not guaranteed.

Jiahui Huang in my group later discovered a much safer process[28] by using gold clusters smaller than 2 nm in diameter and with water as a gas-phase promoter. If we can determine the specific number of gold atoms in the clusters together with suitable support materials, we will be able to improve the conversion and selectivity to the commercially required level.

## *Selective Hydrogenation: Dissociation of Hydrogen Molecule at Perimeter Interfaces*

Another major question is whether gold catalysts are capable of hydrogenation reactions. This is because the dissociation of hydrogen molecules is very slow on gold surfaces.[29] Tadahiro Fujitani, a leader in my research group, studied the $H_2$–$D_2$ exchange reaction by using model Au/$TiO_2$ (110) catalysts.[30] As shown in Figure 5, the rate of HD formation for catalyst samples (with the same gold loading) increases exponentially with a decrease in the diameter of gold particles. In contrast, the turnover frequency, the rate of HD formation per perimeter gold atom, is independent of the diameter of the gold particles, which means that the reaction rate is proportional to the length of the perimeter and indicates that the perimeter is the location of dihydrogen dissociation. This mechanism motivates us to increase the perimeter length by minimizing the diameter of the gold NPs and to select suitable metal oxide supports.

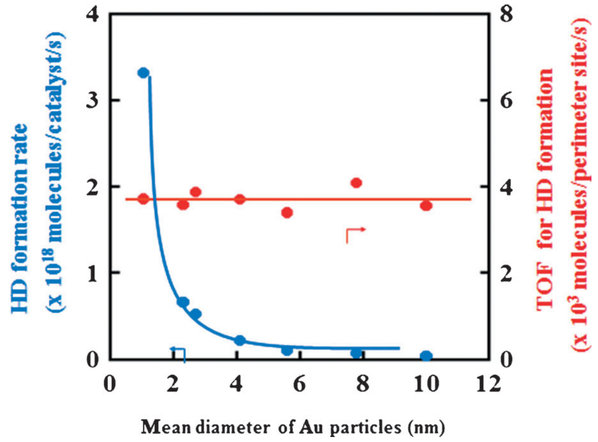

*Figure 5.* Rates of $H_2$–$D_2$ exchange on Au/$TiO_2$(110) model catalysts as a function of the mean diameter of gold nanoparticles.

## The Bright Future of Gold Catalysis: Size Specificity in Clusters

Figure 6 shows that the number of papers dealing with "gold catalysts and catalysis" began to increase slowly since Hutchings[31] and we[9] independently reported in the middle of 1980s the remarkably high catalytic activity of auric chloride in acetylene hydrochlorination and of composite oxides of gold with 3d transition metals in the low-temperature oxidation of CO, respectively. The second burst of research activity was ignited in the late 1990s by the findings of selective oxidations. In 1998 Prati and Rossi reported that polyalcohols could be oxidized with molecular oxygen to carboxylic acids in aqueous alkali solutions[32] and Hayashi et al. reported the gas-phase propylene epoxidation with $O_2$ and $H_2$.[26] These findings made a great impact on chemistry-related communities in academia and industry, resulting in an exponential increase in the number of published papers. Now the third wave is coming, about 1600 papers a year, triggered by the reports of selective hydrogenations and by gold clusters. About half of the papers concerned gold NPs and clusters (orange bars); the other half (green bars) deals with gold except for NPs and clusters, for example, bulk gold, colloidal gold, porous gold, and organic gold complexes. Homogeneous gold catalysts constitute the second expanding wing of gold catalysis.[33–36] In particular, perfect selectivity has been obtained by gold complexes in some hydrogenation reactions.[33–35]

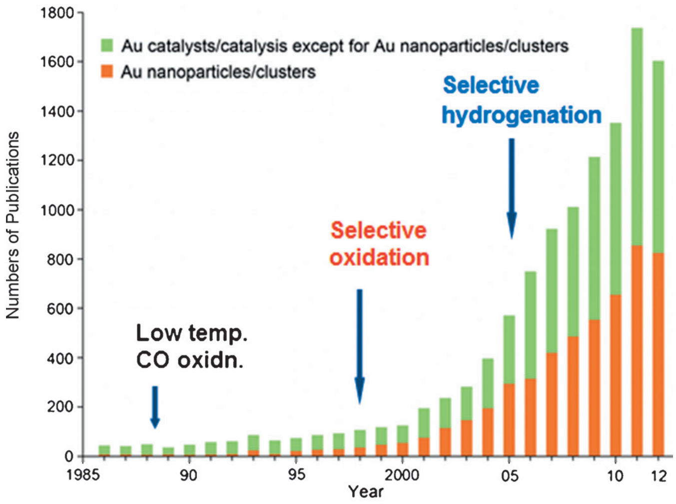

*Figure 6.* Remarkable increase in the number of papers dealing with gold catalysts and catalysis published between 1985 and 2012.

Gold clusters smaller than 2 nm in diameter, composed of less than 200 atoms, may display unprecedented catalyst properties[37] such as size specificity,[38] perfect selectivity, surprisingly high activity,[39] and practical stability.[40] The band structures of gold clusters are different from the bulk.[17] As seen in Figure 7, in the icosahedron composed of 147 atoms, coordinatively unsaturated sites such as corners and edges make up 49% of the total gold atoms and the surface-exposed gold atoms account for 63%. Since the influence of support materials will be much more intense than in the case of gold NPs, the catalytic properties and reactivity of gold clusters will become an exciting area of research.

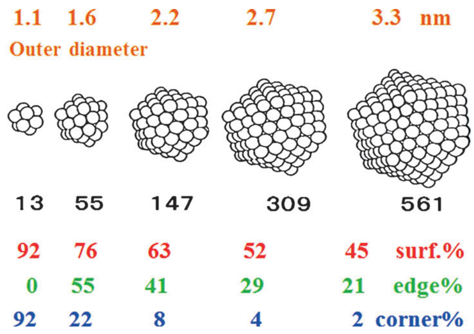

*Figure 7.* Outer diameters and the percentages of surface-exposed atoms, edge atoms, and corner atoms in icosahedron clusters.

Commercial applications of gold catalysis and catalysts have flourished since 2012, when the Sixth International Conference on Gold Science, Technology and its Applications was held in Tokyo (September 5–8, 2012). We accepted 391 participants, which was about 10% more than those at the preceding conference in Heidelberg in 2009. The major topics were the preparation and installation of gold NPs and their applications to electronics, optics, medicinal diagnosis and care, and catalysts.

Pd-Au bimetallic catalysts are used for the treatment of diesel engine exhaust gas by Fiat in Italy[41] and for groundwater treatment (transformation of organic chlorinated compounds such as chloroform to methane) by DuPont in USA. Gold NPs on PET (polyethylene terephthalate) nonwoven fabric and alumina woven mesh have been developed for air purification by NBC Meshtec Inc. in Japan.[42] Asahi Kasei Chemicals has been running a commercial plant to produce methyl methacrylate from methacrolein by using a Au/NiO/$SiO_2$-$Al_2O_3$-MgO catalyst since 2008.[43]

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