Gold Catalysts

DOI: 10.1002/anie.200701622

Gold Catalysts: Towards Sustainable Chemistry

*Tamao Ishida and Masatake Haruta**

Keywords:
gold · oxidation · polymers · supported catalysts · sustainable chemistry

Sustainable development is an important theme in the 21st century.[1] Global warming appears to be steadily ongoing, and the consumption of fossil fuels is accelerated owing to the rapid economic growth in Asian countries. Since the first oil crisis in 1973, tremendous efforts have been made in industrial sectors to save energy and resources. In particular, the chemical industry achieved the largest reduction in energy consumption, down by 50 % in 1983 with respect to that in 1973. However, since 1984, no further improvements have been attained. This "dead rock" implies that technological innovations are vital to break it. In the production of fine chemicals such as food additives, cosmetics, and surfactants, the generation of unwanted by-products exceeds that of desired products in quantity. The so-called E factor (defined as the weight of by-products divided by the weight of desired products) is in the range of 5–10. Stoichiometric reactions should be replaced by simple catalytic reactions that require the minimum of energy.

A key technology which is bringing a breakthrough is catalysis by gold nanoparticles and clusters.[2] Most recently, Kobayashi and co-workers demonstrated the great potential of polymer-supported gold as catalysts for greener liquid-phase selective oxidation processes.[3] Precisely speaking, their catalysts are not new in terms of solid-polymer-supported gold catalysts, and there is still room for simplifying the method of preparation of gold catalysts. However, they obtained higher catalytic performances for gold supported on polymers than for gold on metal oxides by simultaneous optimization of the support, solvents, and size of gold particles.

Gold was earlier considered to be chemically inert and regarded as a poor catalyst. However, when gold is prepared as very small particles with diameters of less than 10 nm and is highly dispersed on metal oxides, it turns to be a highly active catalyst for many reactions such as CO oxidation and propylene epoxidation in the gas phase.[4]

Over the last decade, much attention has been paid also to the activity of gold catalysts in the liquid phase owing to the pioneering work by Prati, Rossi et al.[5] The ideal "green" processes are carried out at atmospheric pressure and room temperature, in aqueous media or under solvent-free conditions, and using air as oxidant or molecular hydrogen as reductant. Gold nanoparticles supported on activated carbon or metal oxides are active for some liquid-phase reactions such as the selective oxidation of alcohols into the corresponding aldehydes, ketones, or carboxylic acid with molecular oxygen in aqueous media, and selective reduction of nitro arenes into amino arenes with hydrogen.[15] In most cases, gold catalysts showed high catalytic activity with much higher selectivity at lower temperature and stability than for palladium and platinum catalysts.

The selective oxidation of glucose by gold supported on activated carbon or metal oxides[6] has been a very active research area, as the transformation of readily available glucose to valuable gluconic acid is of great importance. In fact, gold catalysts supported on activated carbon and Al_2O_3 worked efficiently under moderate conditions (e.g. atmospheric pressure, using molecular oxygen as oxidant, and reaction temperatures of 303–333 K). In the case of Au on activated carbon, turnover frequencies (TOF) reached high values (12 500 to 25 000 h^{-1}) and high selectivities to gluconic acid were observed ranging from 92 to 99 % by varying the kind of activated carbon.[6b]

Recently, Corma and co-workers have reported that Au nanoparticles (2–5 nm) supported on nanocrystalline CeO_2 (ca. 5 nm) gave a highly active, selective, and recyclable catalyst for the oxidation of alcohols using molecular oxygen at atmospheric pressure under solvent-free and base-free conditions.[7] The TOF value for oxidation of 1-phenylethanol (12 480 h^{-1}) exceeded that of Pd nanoparticles supported on hydroxyapatite (9800 h^{-1}), which was reported by Kaneda and co-workers.[8] In addition, Au/CeO_2 showed a much higher selectivity for the oxidation of allylic alcohols to unsaturated ketones. For example, the oxidation of 1-octen-3-ol yielded 1-octen-3-one as a main product in the presence of Au/CeO_2 with a selectivity of 93 %, while Pd/CeO_2 revealed a selectivity of 58 % because of the promotion of isomerization and hydrogenation of the carbon–carbon double bond to yield saturated ketones as a by-product.[7b] Moreover, Au on activated carbon and Au/Al_2O_3 preferentially accelerate the

---

[*] Dr. T. Ishida, Prof. Dr. M. Haruta
Department of Applied Chemistry
Graduate School of Urban Environmental Sciences
Tokyo Metropolitan University
1-1 Minami-osawa, Hachioji
Tokyo 192-0397 (Japan)
Fax: (+81) 42-677-2851
E-mail: haruta-masatake@center.tmu.ac.jp
and
Japan Science Technology Agency (JST), CREST
4-1-8 Hon-chou, Kawaguchi
Saitama, 332-0012 (Japan)

oxidation of the hydroxy group in 2-aminopropanol to yield 2-aminopropanoic acid and avoid the oxidation of the amino group.[9] This result indicates an attractive selectivity for functional groups in liquid-phase aerobic oxidations.

During the course of research and development into liquid-phase reactions, the supports of interest have shifted from activated carbon and metal oxides to organic polymers as a stabilizing agent or a solid support for gold nanoparticles. Tsukuda and co-workers[10] prepared small gold clusters (1.3 nm diameter) stabilized by poly(*N*-vinylpyrrolidone) (Au:PVP; Figure 1 a) and reported that these gold clusters catalyzed the carbon–carbon bond formation of phenylboronic acid and the oxidation of benzyl alcohol into benzaldehyde as the main product and benzoic acid as a by-product in water at 303 K using molecular oxygen as oxidant. They reported the size-specific catalytic activity of Au:PVP; that is, the TOF value increased gradually with a decrease in the diameter of the Au nanoparticles from 6 nm to 3 nm and then it rose dramatically at diameters below 3 nm. However, taking industrial use into account, a heterogeneous catalytic system would be advantageous in terms of recyclability.

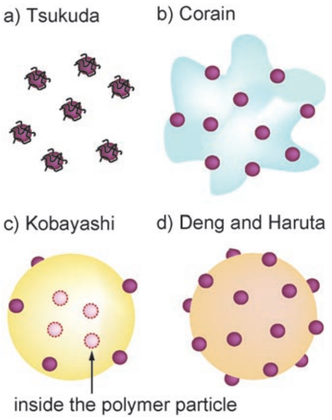
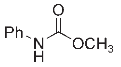
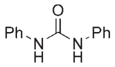
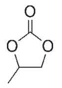
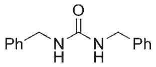


Figure 1. Four examples of polymer-stabilized gold nanoparticles and clusters: a) Gold clusters stabilized by water-soluble polymers, b) gold nanoparticles immobilized in the pores of a functionalized resin, c) gold clusters supported inside a polymer particle, and d) gold nanoparticles deposited on polymer surfaces.

The first example of a polymer-supported gold catalyst was provided by Shi, Deng et al,[11] who used a cation-exchange resin as a polymer support after pretreatment with NaOH. Impregnation of the resin with $HAuCl_4$ followed by drying at 333 K or at room temperature afforded gold nanoparticles supported on the resin (Figure 1 d). As the gold nanoparticles were deposited without calcination in air at higher temperatures, the gold might not be fully decomposed into metallic Au particles from Au^{3+} species. The obtained supported gold catalyst was applied to the formation of urea and carbamates from amines using carbon monoxide and molecular oxygen in the absence or presence of methanol, respectively (Table 1, entries 1 and 2). The catalytic activity was strongly affected by the pretreatment of the ion-exchange resin. On the other hand, gold nanoparticles (< 10 nm) supported on an anion-exchange resin catalyzed the insertion reaction of CO_2 with epoxides to yield cyclic carbonates (Table 1, entry 3) and the formation of ureas from amines with CO_2 (Table 1, entry 4).

Corain, Prati, and co-workers reported well-defined gold nanoparticles supported by a gel-type polyacrylic resin, poly-2-(methylthio)ethyl methacrylate-*N*,*N*-dimethyl acrylamide-*N*,*N*-methylene bisacrylamide (MTEMA-DMAA-4–8; Figure 1 b).[12] The thioether (R-S-R) functional group was used as a coordination site for a Au precursor prior to its reduction to Au^0 with $NaBH_4$. The gel-type resin had small pores with a mean diameter of 2.5 nm, while the size of the obtained gold nanoparticles was 2.2 nm. The slightly smaller size of the nanoparticles relative to the pore size of the polymer gel suggested that the cavities in the polymer gel prevented the gold nanoparticles from aggregating. The gold nanoparticles supported on the gel-type polymer catalyzed the oxidation of

Table 1: Representative reactions catalyzed by polymer-supported Au nanoparticles.

Entry	Support	Particle size [nm][a]	Substrate	Product	Substrate/ Au ratio	Yield [%][b]	Selectivity [%]	TOF [h^{-1}]	Ref.
1[c]	cation-exchange resin	< 10	aniline		540	95	> 99	530	[11a]
2[c]			aniline		6370	70	99	1475	[11a]
3[d]	anion-exchange resin	3–9			563 000	53	n.d.[e]	57 900	[11b]
4[f]			benzylamine		72 900	83[g]	n.d.[e]	3000[h]	[11b]
5[i]	MTEMA-DMAA-4–8	2.2	1-pentanol	1-pentanal	1000	25	66	n.d.[e]	[12]
6[i]			1-pentanal	1-pentanoic acid	1000	95	n.d.[e]	n.d.[e]	[12]
7[j]	polystyrene-based copolymer	> 1	1-phenylethanol	actophenone	1640	6	n.d.[e]	20 000	[3]
8[k]	anion-exchange resin	2.6	glucose	gluconic acid	32 000	98[l]	n.d.[e]	33 300	[14]

[a] Observed by transmission electron microscopy. [b] GC yield. [c] MeOH (for carbamate synthesis), $pCO = 4$ MPa, $pO_2 = 1$ MPa, 175 °C, 1 h. [d] $pCO_2 = 3$ MPa, 150 °C, 5 h. [e] n.d. indicates no data. [f] $pCO_2 = 5$ MPa, 180 °C, 20 h. [g] Yield of isolated product. [h] Turnover frequencies for products (mol product per mol Au per hour). [i] $pO_2 = 0.3$ MPa, 70 °C, 2 h. [j] $pO_2 = 0.1$ MPa, 160 °C, 0.5 h. [k] $pO_2 = 0.1$ MPa, 60 °C, 2 h. [l] Determined by titration with aqueous NaOH.

pentanol to pentanal (25 % conversion; Table 1, entry 5) and of pentanal to pentanoic acid (95 % conversion; Table 1, entry 6). These performances, however, were still inferior to that of Au/CeO_2.

The most recent example of polymer-supported gold catalysts came from Kobayashi and co-workers, who developed recyclable polystyrene-based copolymer-microencapsulated gold nanocatalysts (PI-Au), in which gold nanoparticles were stabilized by benzene rings in the polystyrene moiety (Figure 1 c).[3] These PI-Au catalysts were active at room temperature when using the appropriate combination of water, organic solvent, and base. Hutchings and co-workers had previously studied solvent effects on the selective oxidation of cyclohexene over Au on activated carbon,[13] and the highest selectivity for cyclohexene oxide (50 %) was obtained in 1,2,3,5-tetramethylbenzene, while 2-cyclohexen-1-one was obtained as a main product (78 % selectivity) in 1,3,5-trimethylbenzene at 353 K. Kobayashi and co-workers' results have shown that further optimization of reaction media could lead to the use of milder conditions, such as room temperature. They also examined the solvent-free oxidation of 1-phenylethanol at 433 K under almost the same reaction conditions (at atmospheric pressure) as employed by Corma and co-workers.[7] The TOF value for PI-Au was recorded as 20 000 h^{-1}, which exceeded that for Au/CeO_2 (12 480 h^{-1}).[7b]

Recently, we have developed a simple technique to prepare polymer catalysts by using surface functional groups on an anion-exchange resin as a reducing agent.[14] The obtained Au/polymer catalysts exhibit a higher TOF (33 000 h^{-1}) than that of Rossi and co-workers' Au/activated carbon catalyst in the oxidation of glucose to gluconic acid in water.[6b]

The four above-mentioned examples of Au/polymer catalysts (Figure 1) prove that functionalized organic polymers not only work as a support to stabilize small gold nanoparticles but also help to achieve higher catalytic activity than conventional gold catalysts using metal oxides and activated carbon as support materials.

Despite the recent progress, the reaction mechanism involving the functionalized group in the polymer backbone and the size effect of gold nanoparticles remain unclear. In the case of Au/CeO_2, the proposed reaction mechanism involves cationic gold species and Ce^{3+}, and the oxygen-deficient sites of CeO_2 are assumed to play an important role for physisorption of molecular oxygen. What role does the polymer play in the gel-catalyzed reaction mechanism (it has no oxygen-deficient sites)? Additionally, the production of small gold clusters with diameters of less than 2 nm, which is a critical size for a dramatic change in electronic structure, is still an exciting area of research. These small clusters composed of less than 300 atoms can be tuned more pronouncedly by choosing support materials ranging from metal oxides and activated carbon to polymers. The success of Kobayashi's group to control the size of gold particles down to 1 nm through polymer incarceration will surely present a key stepping stone toward the goal of sustainable chemistry.

---

[1] a) G. A. Olah, *Angew. Chem.* **2005**, *117*, 2692; *Angew. Chem. Int. Ed.* **2005**, *44*, 2636; b) N. Armaroli, V. Balzani, *Angew. Chem.* **2007**, *119*, 52; *Angew. Chem. Int. Ed.* **2007**, *46*, 52.

[2] A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem.* **2006**, *118*, 8064; *Angew. Chem. Int. Ed.* **2006**, *45*, 7896.

[3] H. Miyamura, R. Matsubara, Y. Miyazaki, S. Kobayashi, *Angew. Chem.* **2007**, *119*, 4229; *Angew. Chem. Int. Ed.* **2007**, *46*, 4151.

[4] M. Haruta, *Chem. Rec.* **2003**, *3*, 75.

[5] a) L. Prati, M. Rossi, *J. Catal.* **1998**, *176*, 552; b) S. Biella, L. Prati, M. Rossi, *J. Catal.* **2002**, *206*, 242.

[6] a) N. Thielecke, M. Aytemir, U. Prüsse, *Catal. Today* **2007**, *121*, 115; b) M. Comotti, C. Della Pina, R. Matarrese, M. Rossi, A. Siani, *Appl. Catal. A* **2005**, *291*, 204.

[7] a) A. Abad, P. Concepción, A. Corma, H. García, *Angew. Chem.* **2005**, *117*, 4134; *Angew. Chem. Int. Ed.* **2005**, *44*, 4066; b) A. Abad, C. Almela, A. Corma, H. García, *Tetrahedron* **2006**, *62*, 6666; c) A. Abad, C. Almela, A. Corma, H. García, *Chem. Commun.* **2006**, 3178.

[8] K. Mori, T. Hara, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.* **2004**, *126*, 10657.

[9] S. Biella, G. L. Castiglioni, C. Fumagalli, L. Prati, M. Rossi, *Catal. Today* **2002**, *72*, 43.

[10] a) H. Tsunoyama, H. Sakurai, N. Ichikuni, Y. Negishi, T. Tsukuda, *Langmuir* **2004**, *20*, 11293; b) H. Tsunoyama, H. Sakurai, N. Ichikuni, Y. Negishi, T. Tsukuda, *J. Am. Chem. Soc.* **2005**, *127*, 9374; c) H. Tsunoyama, H. Sakurai, T. Tsukuda, *Chem. Phys. Lett.* **2006**, *429*, 528.

[11] a) F. Shi, Y. Deng, *J. Catal.* **2002**, *211*, 518; b) F. Shi, Q. Zhang, Y. Ma, Y. He, Y. Deng, *J. Am. Chem. Soc.* **2005**, *127*, 4182.

[12] C. Burato, P. Centomo, G. Pace, M. Favaro, L. Prati, B. Corain, *J. Mol. Catal. A* **2005**, *238*, 26.

[13] M. D. Hughes, Y.-J. Xu, P. Jenkins, P. McMorn, P. Landon, D. I. Enache, A. F. Carley, G. A. Attard, G. J. Hutchings, F. King, E. H. Stitt, P. Johnston, K. Griffin, C. J. Kiely, *Nature* **2005**, *437*, 1132.

[14] T. Ishida, M. Haruta, R. Makiyama, Patent JP 2007-082287, **2007**.

[15] A. Corma, P. Serna, *Science* **2006**, *313*, 332.