DOI: 10.1002/ange.200802845

Gold Nanoparticles

Influence of the Support and the Size of Gold Clusters on Catalytic Activity for Glucose Oxidation**

*Tamao Ishida, Naoto Kinoshita, Hiroko Okatsu, Tomoki Akita, Takashi Takei, and Masatake Haruta**

Dedicated to the Catalysis Society of Japan on the occasion of its 50th anniversary

Gold was neglected as a catalytic metal in the history of heterogeneous catalysis for more than 100 years. However, when gold is deposited as nanoparticles (NPs) on basic transition-metal oxides, it exhibits unique catalytic performance, for example, the catalysis of the oxidation of carbon monoxide at a temperature as low as $-70\,°C$.[1]

As conventional impregnation does not lead to the high dispersion of small gold NPs, several methods for catalyst preparation have been developed.[1] One of the most frequently used techniques is the deposition–precipitation (DP) method, in which $Au(OH)_3$ embryos generated from $HAuCl_4$ by treatment with NaOH are precipitated and deposited exclusively on the surfaces of basic metal oxides; these deposits are then transformed into gold NPs with diameters smaller than 5 nm by calcination.[1,2] Modified catalyst-preparation methods, such as DP urea, in which urea is used instead of NaOH as the precipitating agent,[3] and the incipient wetness method[4] have also been used. However, these methods are not applicable to supports that have a low point of zero charge, such as acidic metal oxides (e.g. SiO_2-Al_2O_3), carbon materials, and organic polymers. Accordingly, gold colloids prepared beforehand were immobilized by mixing with carbon to produce carbon-supported gold catalysts.[5] Therefore, other new versatile methods are required for the direct deposition of Au clusters from Au precursor compounds onto various kinds of support materials.

The catalytic transformation of biomass-derived natural resources into valuable compounds is of great importance for sustainable developments.[6] In particular, the aerobic oxidation of glucose to gluconic acid over transition-metal catalysts, including Pd, Pt, and Au, has been studied during the last two decades.[4,7–12] Gold catalysts for this transformation have been studied extensively,[4,9–12] as Rossi and co-workers reported that gold NPs supported on activated carbon (AC) showed high catalytic activity and high selectivity in the oxidation of glucose to gluconic acid in 2002.[8] The reaction conditions, the reaction mechanism on Au/AC[9a] and Au colloids,[10] the effect of the size of the gold particles,[9b] reproducibility and the durability of Au catalysts,[11] and the preparation of the catalyst[4] have been investigated intensively. However, these approaches are limited to unsupported Au colloids and Au NPs supported on AC, TiO_2, and Al_2O_3.

Recently, we developed a new preparation method, solid grinding (SG), by using a volatile organogold complex, $[Me_2Au(acac)]$ (acac = acetylacetonate), and succeeded in depositing Au clusters smaller than 2 nm in diameter onto porous coordination polymers.[13] We deposited Au clusters onto several kinds of metal oxides and carbon supports by this SG method. Herein we report on the effects of the support and the size of the particles on glucose oxidation over various supported Au catalysts, which were prepared by two methods, DP and SG.

The size of Au particles depended strongly on the preparation method. The deposition–precipitation method could stabilize Au NPs on ZrO_2 (with a mean diameter of 3.7 nm), TiO_2 (2.9 nm), and CeO_2 (4.0 nm). However, large Au NPs were formed simultaneously with small Au NPs on Al_2O_3, so that a mean diameter of 4.3 nm was observed.

In the SG method, $[Me_2Au(acac)]$ and the carbon supports AC, which is microporous, and nanoporous carbon (NPC), which has 2 nm mesopores and hollow cores, were ground in an agate mortar and in a ball mill (300 rpm), respectively, in air at room temperature for 20 to 30 min and then subjected to calcination at 300 °C for 4 h. Solid grinding gave Au clusters and small NPs deposited on the carbon supports, especially on NPC. The mean diameters of the Au particles on NPC were calculated by HAADF STEM (high-angle annular dark-field scanning transmission electron microscopy) and TEM to be 1.9 and 2.6 nm, respectively (Figure 1 a,b).

During the optimization of the grinding conditions, we found that ball milling (350 rpm for 1 h) was favorable for metal oxides in contrast to organic polymers and carbon

---

[*] Dr. T. Ishida, N. Kinoshita, H. Okatsu, Prof. Dr. T. Takei,
Prof. Dr. M. Haruta
Graduate School of Urban Environmental Sciences
Tokyo Metropolitan University (TMU)
1-1 Minami-osawa, Hachioji, Tokyo 192-0397 (Japan)
Fax: (+81) 42-677-2851
E-mail: haruta-masatake@center.tmu.ac.jp

Dr. T. Ishida, N. Kinoshita, H. Okatsu, Dr. T. Akita, Prof. Dr. T. Takei,
Prof. Dr. M. Haruta
Japan Science and Technology Agency (JST), CREST
4-1-8 Hon-cho, Kawaguchi, Saitama 332-0012 (Japan)

Dr. T. Akita
Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST)
1-8-31 Midorigaoka, Ikeda, Osaka 563-8577 (Japan)

[**] We thank Y. Misaki of TMU for TEM observation and T. Hara of Fuso Chemical Co. for HPLC analysis. This research was supported financially by JST, CREST, and the Gold Research Opportunities Worldwide (GROW) program of the World Gold Council.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200802845.

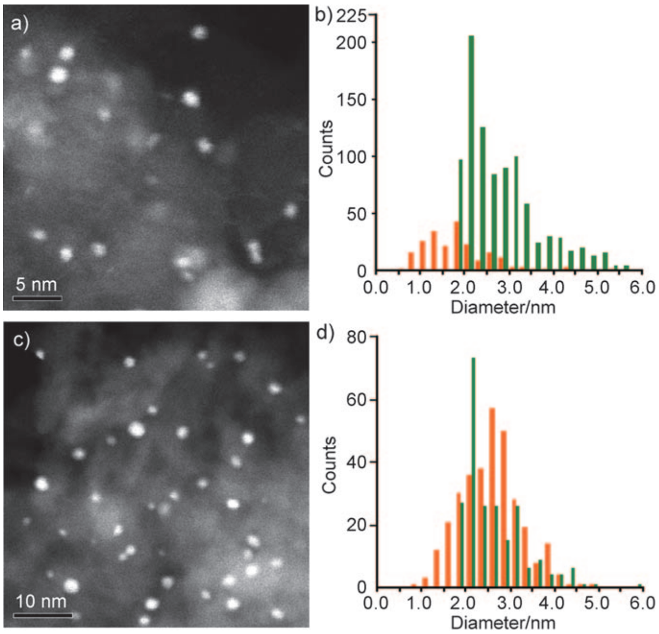

Figure 1. HAADF STEM images of a) Au/NPC (SG) and c) Au/Al_2O_3 (SG), and the size distribution of Au particles on b) NPC and d) Al_2O_3. Orange and green bars indicate data obtained from HAADF STEM and TEM images,[14] respectively.

materials. It is likely that harder metal-oxide particles needed stronger mixing than soft carbon materials. Uniform grinding partially failed in a ball mill, in which large Au NPs were formed simultaneously with Au clusters in the completely solid state. Therefore, acetone was used for uniform milling to prevent the aggregation of Au particles. The mean diameter of Au particles on Al_2O_3 was calculated to be 2.6 nm by TEM and HAADF STEM (Figure 1 c,d).

Guzman and Gates reported the reaction of [$Me_2Au(acac)$] with Al_2O_3 upon mixing as slurry in hexane.[15] Mixing had to be carried out under a completely inert atmosphere owing to the instability of [$Me_2Au(acac)$], and the reaction took one day under these conditions. In contrast, milling enables the reaction time to be shortened by enhancing the reaction in air. [$Me_2Au(acac)$] was not reduced on nonconductive Al_2O_3, ZrO_2, and carbon materials during grinding.

Solid grinding, both in the completely solid state and in an acetone slurry, was found to be an efficient technique for the preparation of Au clusters on nonconductive Al_2O_3, ZrO_2, and carbon supports, but unsuitable for semiconductive supports, in particular, TiO_2. Guzman and Gates also investigated the mechanism of the ligand exchange of [$Me_2Au(acac)$] with the surface hydroxy groups of Al_2O_3 (step 1 in Figure 2 a).[15] In our experiments, the Au^{III} precursors adsorbed on Al_2O_3 as a result of ball milling were stable in air for 1 h. They were then reduced to form Au^0 clusters by calcination (step 2 in Figure 2 a). Some fractions of the Au^{III} precursors adsorbed on TiO_2 and CeO_2, however, might be reduced by the support at the M^{3+} cation radical or oxygen radical sites on the surfaces during ball milling in air (steps 2 and 3 in Figure 2 b). This hypothesis would explain the observed color change from white to mauve. Once Au^0 seed crystals had formed on the supports, they enhanced the reduction of Au^{III} on the surface of the gold seed crystals and thus caused the growth of large Au NPs. Although the size of the Au particles formed by SG and DP was similar for CeO_2, a smaller amount of Au^{III} precursors could be adsorbed onto CeO_2 by SG than the DP.

The catalytic performance of the supported gold nanoparticles was first tested for the oxidation of CO in the gas phase (Figure 3). Solid grinding was advantageous over DP for the preparation of Au/Al_2O_3 and Au/ZrO_2 owing to the smaller size of the Au particles. However, the nature of the support affected the catalytic activity more strongly. Lower catalytic activity was observed with nonreducible Al_2O_3 than with reducible metal oxides, such as ZrO_2, TiO_2, and CeO_2, which can form oxygen-vacancy sites at the perimeter interfaces of Au particles. Gold NPs exhibited no catalytic activity at all at temperatures up to 120 °C when they were deposited on carbon materials and polymers. Similarly, no catalytic activity was observed for gold NPs on carbon supports and polymers in the gas-phase oxidation of H_2.

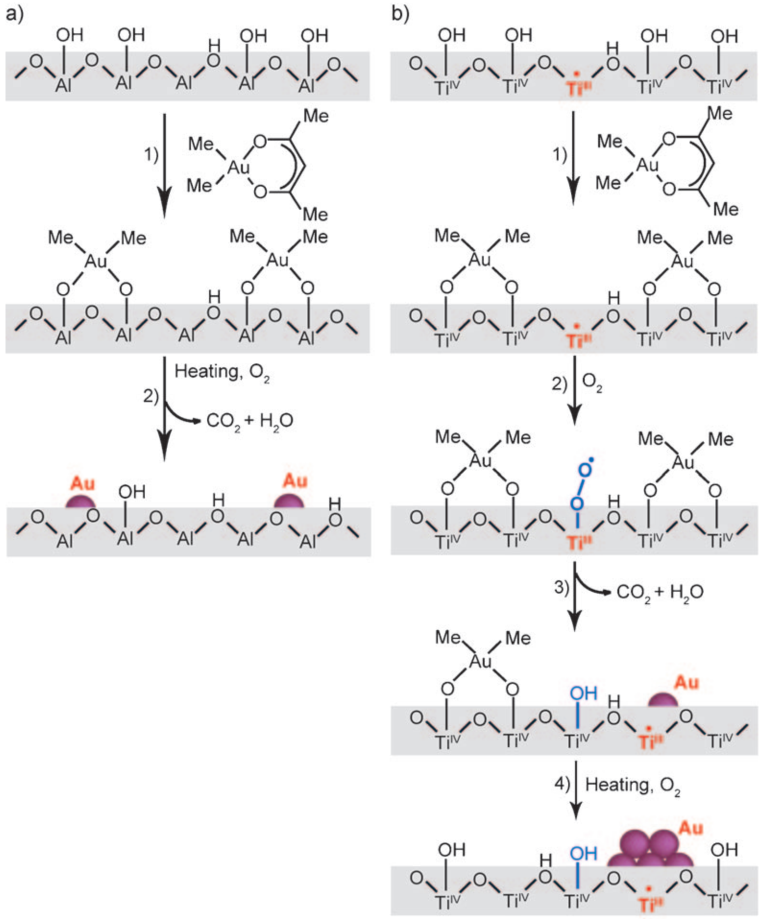

Figure 2. Probable pathways for the reaction of [$Me_2Au(acac)$] with a) Al_2O_3 and b) TiO_2 to form Au particles.

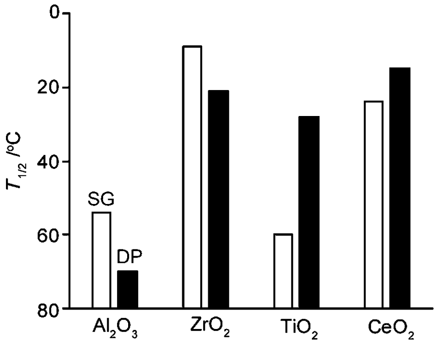

Figure 3. Comparison of the catalytic activities of metal-oxide-supported Au NPs prepared by SG and DP. $T_{1/2}$ is the temperature for 50% conversion in the gas-phase oxidation of CO. Reaction conditions: CO (1 vol%) in air, Au catalyst (150 mg), space velocity: 20000 mL g_{cat}^{-1} h^{-1}.

Next, the oxidation of glucose was studied by bubbling oxygen through a 5 wt% aqueous solution of glucose at a flow rate of 120 mL min^{-1} at 50°C and pH 9.0 in the presence of Au catalysts under ambient pressure. In contrast to CO oxidation, the catalytic activity observed for glucose oxidation over Au catalysts was influenced more significantly by the size of the Au particles than by the nature of the support, as indicated by the turnover frequency (TOF) per surface Au atom (Figure 4). The selectivity for the formation of gluconic acid was always very high at above 98%.

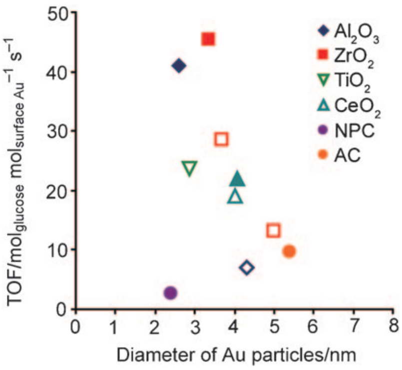

Figure 4. Turnover frequencies for glucose oxidation (glucose reacted (mol) per number of surface Au atoms (mol) per second) versus the diameter of the Au particles. Filled and open symbols indicate samples prepared by SG and DP, respectively. Reaction conditions: 5 wt% glucose solution (175 mL), Au catalyst (30 mg), O_2 (120 mL min^{-1}), 50°C, pH 9.0.

The highest catalytic activity was observed for Au/ZrO_2 (SG), with a turnover frequency of 45 $mol_{glucose}$ $mol_{surface\ Au}^{-1}$ s^{-1} at 50°C and pH 9.0. The highest TOF per surface Au atom reported to date was 42 s^{-1} at 50°C and pH 9.5.[9d] As the reaction rate of glucose oxidation increases with an increase in pH,[8] the TOF of Au/ZrO_2 (SG) reached 56 s^{-1} at 50°C and pH 9.5. To the best of our knowledge, this value is the highest reported to date for glucose oxidation catalyzed by gold NPs.

Comotti et al. reported that the catalytic activity of Au NPs for glucose oxidation was detectable only when Au was smaller than 10 nm and that it was inversely proportional to the diameter of the Au particles in the range of 3–6 nm.[9b] This result indicates that the catalytic activity per surface Au atom is independent of the diameter of the Au particles. In contrast, metal-oxide-supported Au catalysts in this study showed an increase in TOF with a decrease in the diameter of the Au particles. Although the size dependencies of the TOF values in our study and that of Commoti et al. were different, the size of the Au particles appears to be the most important parameter. Glucose oxidation in the liquid phase may occur at the Au surfaces rather than at the perimeter interfaces between Au particles and the supports, in contrast to the gas-phase CO oxidation.[1]

The rate of glucose oxidation is expressed by Equation (1):.

$$r = k[\text{glucose}]^a\,[O_2]^b = k'[\text{glucose}]\ \ (k' = k[O_2]^b) \qquad (1)$$

The reaction was estimated to be 0.4 order with respect to glucose for Au/Al_2O_3 and 1.0 order for Au/NPC in the presence of excess oxygen.[14] Beltrame et al. reported zero- and first-order dependence on glucose and oxygen, respectively, for unsupported Au colloids.[10] However, at lower glucose concentrations, when oxygen was present in excess relative to glucose, the reaction order with respect to glucose became close to 0.4,[10] the value estimated for the reaction with our Au/Al_2O_3 catalyst.

We derived Arrhenius plots for the temperature range from 40 to 70°C.[14] The catalytic activity of Au/Al_2O_3 was comparable to that of Au/ZrO_2 (DP) and slightly higher than that of Au/carbon at 70°C. However, Au/Al_2O_3 maintained a higher catalytic activity than that of Au/ZrO_2 (DP) at lower temperature. The apparent activation energies were calculated to be 27, 53, 72, and 96 kJ mol^{-1} for Au supported on Al_2O_3 (SG), ZrO_2 (DP), NPC (SG), and AC (SG), respectively. The apparent activation energy for glucose oxidation over unsupported Au colloids was reported to be 47 kJ mol^{-1}.[10] The activation energies differed according to the nature of the support and tended to be lower for Au on metal oxides. The catalytic activity of Au/carbon was depressed appreciably at temperatures below 50°C. It can be assumed that carbon materials participate in only weak or no metal–support interactions[9b] and adsorb glucose to a certain extent owing to the large specific surface area. These features may explain the stronger dependence of the reaction rate on glucose concentration and the reaction temperature with carbon supports than with metal-oxide supports. In contrast, metal-oxide supports might affect Au clusters electronically; such effects may lead to the weaker rate dependencies than those observed with Au/carbon and unsupported Au colloids.

In summary, we have explored simple but efficient methods for the preparation of small Au NPs on a variety of support materials. In particular, the solid grinding (SG) of a volatile organogold complex with a nonreducible support can lead to the formation of Au clusters that exhibit excellent catalytic performance in the oxidation of glucose. We have reached the following conclusions:

1) The catalytic mechanism of Au seems to be completely different for gas-phase and liquid-phase oxidation reactions. As far as the gas-phase oxidation of H_2 and CO and the liquid-phase oxidation of glucose are concerned, the appropriate selection of the support material is more important for the gas-phase reactions, whereas the control of the size of Au particles is more critical in the liquid phase.
2) For glucose oxidation, the influence of the support and the size of Au NPs was discussed comprehensively for a variety of support materials. Gold on ZrO_2 (SG) exhibited extremely high catalytic activity with TOF values per surface Au atom of 45 s^{-1} at 50 °C, pH 9.0 and 56 s^{-1} at 50 °C, pH 9.5.
3) The most suitable method for Au deposition depends on the support.

Experimental Section

Solid grinding: A metal oxide (3.0 g), [$Me_2Au(acac)$] (50 mg for 1 wt% loading of Au), and acetone (10 g for Al_2O_3) were ground by ball milling (350 rpm) at room temperature for 1 h. The product was reduced by calcination in air at 300 °C for 4 h. Grinding of carbon materials was performed without solvents. The grinding conditions were 300 rpm for 300 min in a ball mill (NPC) and for 30 min in an agate mortar (AC), respectively.

Received: June 16, 2008

Keywords: gold · heterogeneous catalysis · nanoparticles · oxidation · solid grinding

[1] a) M. Haruta, *Chem. Rec.* **2003**, *3*, 75 – 87; b) M. Haruta, *J. New Mater. Electrochem. Syst.* **2004**, *7*, 163 – 172.
[2] *Catalysis by Gold* (Eds.: G. C. Bond, C. Louis, D. T. Thompson), Imperial College Press, London, **2006**.
[3] a) R. Zanella, L. Delannoy, C. Louis, *Appl. Catal. A* **2005**, *291*, 62 – 72; b) R. Zanella, S. Giorgio, C. R. Henry, C. Louis, *J. Phys. Chem. B* **2002**, *106*, 7634 – 7642.
[4] a) C. Baatz, N. Thielecke, U. Prüsse, *Appl. Catal. B* **2007**, *70*, 653 – 660; b) C. Baatz, U. Prüsse, *J. Catal.* **2007**, *249*, 34 – 40.
[5] L. Prati, G. Martra, *Gold Bull.* **1999**, *32*, 96 – 101.
[6] J. N. Chheda, G. W. Huber, J. A. Dumesic, *Angew. Chem.* **2007**, *119*, 7298 – 7318; *Angew. Chem. Int. Ed.* **2007**, *46*, 7164 – 7183.
[7] a) A. Abbadi, H. van Bekkum, *J. Mol. Catal. A* **1995**, *97*, 111 – 118; b) S. Hermans, M. Devillers, *Appl. Catal. A* **2002**, *235*, 253 – 264; c) M. Wenkin, P. Ruiz, B. Delmon, M. Devillers, *J. Mol. Catal. A* **2002**, *180*, 141 – 159.
[8] S. Biella, L. Prati, M. Rossi, *J. Catal.* **2002**, *206*, 242 – 247.
[9] a) M. Comotti, C. Della Pina, E. Falletta, M. Rossi, *Adv. Synth. Catal.* **2006**, *348*, 313 – 316; b) M. Comotti, C. Della Pina, R. Matarrese, M. Rossi, *Angew. Chem.* **2004**, *116*, 5936 – 5939; *Angew. Chem. Int. Ed.* **2004**, *43*, 5812 – 5815; c) M. Comotti, C. Della Pina, R. Matarrese, M. Rossi, A. Siani, *Appl. Catal. A* **2005**, *291*, 204 – 209; d) M. Comotti, C. Della Pina, E. Falletta, M. Rossi, *J. Catal.* **2006**, *244*, 122 – 125.
[10] P. Beltrame, M. Comotti, C. Della Pina, M. Rossi, *Appl. Catal. A* **2006**, *297*, 1 – 7.
[11] a) N. Thielecke, M. Aytemir, U. Prüsse, *Catal. Today* **2007**, *121*, 115 – 120; b) N. Thielecke, K.-D. Vorlop, U. Prüsse, *Catal. Today* **2007**, *122*, 266 – 269; c) A. Mirescu, H. Berndt, A. Martin, U. Prüsse, *Appl. Catal. A* **2007**, *317*, 204 – 209.
[12] a) Y. Önal, S. Schimpf, P. Claus, *J. Catal.* **2004**, *223*, 122 – 133.
[13] T. Ishida, M. Nagaoka, T. Akita, M. Haruta, *Chem. Eur. J.* **2008**, *14*, 8459 – 8460.
[14] See the Supporting Information.
[15] J. Guzman, B. C. Gates, *Langmuir* **2003**, *19*, 3897 – 3903.