

Nonscalable Oxidation Catalysis of Gold Clusters

SEIJI YAMAZOE,^{†,‡} KIICHIROU KOYASU,[†] AND
TATSUYA TSUKUDA^{*,†,‡}

[†]Department of Chemistry, School of Science, The University of Tokyo,
Tokyo 113-0033, Japan, and [‡]Elements Strategy Initiative for Catalysts and
Batteries, Kyoto University, Kyoto 606-8501, Japan

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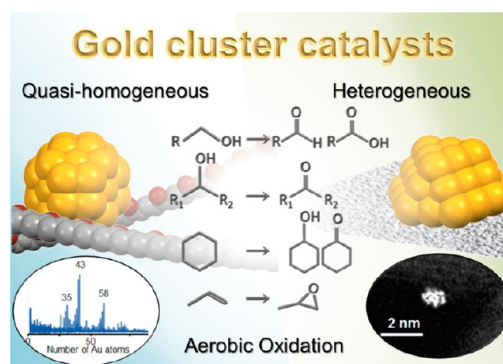
CONSPECTUS

Small, negatively charged gold clusters isolated in vacuum can oxidize CO via electron-transfer-mediated activation of O₂. This suggests that Au clusters can act as aerobic oxidation catalysts in the real world when their structure parameters satisfy given required conditions. However, there is a technical challenge for the development of Au cluster oxidation catalysts; the structural parameters of the Au clusters, such as size and composition, must be precisely controlled because the intrinsic chemical properties of the clusters are strongly dependent on these parameters. This Account describes our efforts to achieve precision synthesis of small (diameter <2 nm) Au clusters, stabilized by polymers and immobilized on supports, for a variety of catalytic applications. Since we aim to develop Au cluster catalysts by taking full advantage of their intrinsic, size-specific chemical nature, we chose chemically inert materials for the stabilizers and supports.

We began by preparing small Au clusters weakly stabilized by polyvinylpyrrolidone (PVP) to test the hypothesis that small Au clusters in the real world will also show size-specific oxidation catalysis. The size of Au:PVP was controlled using a microfluidic device and monitored by mass spectrometry. We found that only Au clusters smaller than a certain critical size show a variety of aerobic oxidation reactions and proposed that the reactions proceed via catalytic activation of O₂ by negatively charged Au clusters.

We also developed a method to precisely control the size and composition of supported Au clusters using ligand-protected Au and Au-based bimetallic clusters as precursors. These small Au clusters immobilized on mesoporous silica, hydroxyapatite, and carbon nanotubes acted as oxidation catalysts. We have demonstrated for the first time an optimal Au cluster size for the oxidation of cyclohexane and a remarkable improvement in the oxidation catalysis of Au₂₅ clusters by single-atom Pd doping.

The non-scalable catalysis of Au clusters that we reported here points to the possibility that novel catalysis beyond that expected from bulk counterparts can be developed simply by reducing the catalyst size to the sub-2 nm regime.



Introduction

Metal Clusters as Novel Catalysts: Opportunities and Challenges. Metal nanoparticles (NPs) have been used as catalysts for the efficient production of useful compounds both in academia and in industry.¹ The major motivation for catalytic applications of metal NPs is twofold: (1) enhancement of the efficiency by increasing the surface-to-volume ratio and the population of low-coordination sites, which are expected to show higher activity than flat surfaces of bulk metals, and (2) control of the selectivity by exposing specific optimal facets for a given catalytic conversion. The basic idea behind these motivations is that the

catalytic properties of NPs can be predicted by those of the corresponding metal surfaces. Thus, enormous effort has been made to control the diameter and morphology of metal NPs.

Metal clusters, defined in this Account as particles with diameters (*d*) smaller than 2 nm or composed of less than 100 atoms, are expected to show novel catalytic properties that are essentially different from those of the corresponding NPs because of the unique geometric and electronic structures (Figure 1). First, the constituent atoms of the metal clusters are arranged in a significantly different manner from that of the bulk metal to reduce the surface energy,

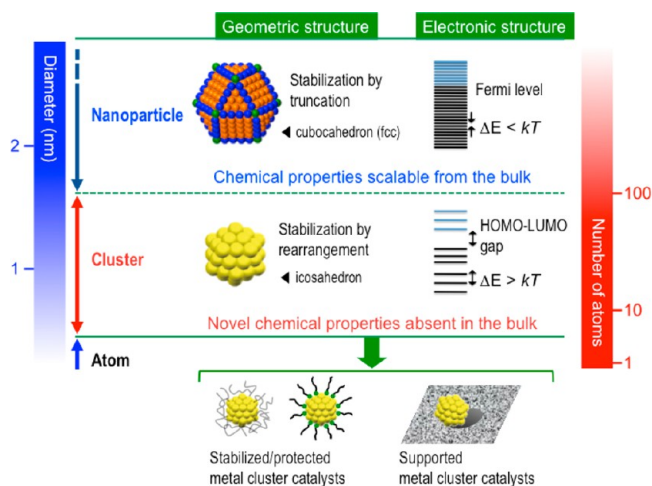


FIGURE 1. Development of novel catalysts based on metal clusters.

whereas a similar reduction is brought about by truncation of the low-coordination site in NPs, as exemplified by the formation of a cuboctahedral motif.² As a result, metal clusters take unique morphologies such as icosahedral and decahedral motifs with 5-fold symmetry.³ The distinct atomic packing in clusters may provide unique reaction sites on the surface. Second, the electronic structures of metal clusters are quantized with an energy gap larger than the thermal energy⁴ so that reactants can be activated via electron transfer from or to the quantized electronic orbitals of the clusters. In contrast, the catalytic properties of metal NPs may not be appreciably affected by the quantized electronic structures because the energy gap between the levels is negligibly small at temperatures typically employed for catalysis.⁵ Third, in addition to the static properties, the dynamic properties will significantly affect the catalysis of metal clusters. The geometrical structure can be readily changed during the catalytic reaction due to exothermicity associated with the adsorption of reactants and chemical reactions.⁶ Moreover, the electronic structure fluctuates with the geometrical isomerization because they are strongly coupled.⁷ Such geometrical and electronic flexibility will open up new reaction pathways having lower activation barriers.

Regardless of the high potential of small metal clusters as novel catalysts, development of metal-cluster-based catalysts in the real world is far from trivial. The primary difficulty lies in their synthesis. Synthesizing metal clusters requires their stabilization against aggregation while part of their surface must be exposed for the catalytic conversion. Thus, we must optimize the trade-off between stability and activity. In addition, the structural parameters of the metal clusters, such as size and composition, must be controlled

at the atomic level because the intrinsic chemical properties of the clusters are strongly dependent on these parameters.⁸

Oxidation Catalysis of Gold Clusters: Aim and Scope of This Account. Another difficulty in the development of metal-cluster-based catalysts is the lack of a guiding principle for a rational design, which forces us to develop catalysts based on a trial-and-error approach. However, in this regard, gold (Au) clusters provide us with an ideal platform. The discovery of Au catalysis by Haruta et al.⁹ stimulated not only the practical development of high-performance Au catalysts in the real world^{10–15} but also fundamental studies on model systems to gain insight into size-specific catalysis. The stability, structures, and chemical properties of bare Au clusters have been studied experimentally and theoretically as a function of size and charge state.^{16–18} As a result, it was revealed that the stability of Au clusters is governed by the electronic structure such that Au clusters with valence electrons totaling 2, 8, 18, 20, 34, 58, and so on gain a special stability because of the closed electronic structure (electronic shell model).^{16,18} The chemical reactivity of Au_n with molecular oxygen, which is related to oxidation catalysis, was also found to be strongly correlated with the electronic structure.^{19–21} As shown in Figure 2,^{16,21} only negatively charged Au_n[–] clusters with an even number of atoms, apart from the *n* = 16 case, react with O₂, whereas other anionic, cationic, or neutral clusters show a much lower reactivity. Since these reactive clusters have a lower electron affinity than nonreactive clusters, it is thought that O₂ is activated by the accommodation of an electron into the lowest unoccupied molecular orbital (LUMO) by these Au cluster anions. Recent photoelectron spectroscopy by Pal et al.²² on the adducts of Au_nO₂[–] provided further insight into the activation mode of O₂: superoxo-like species are produced for *n* = 2, 4, 6, 8, and 20, whereas peroxy-like species are produced for *n* = 8, 12, and 14 (Figure 2). It was pointed out that the peroxy-like species are produced by the Au cluster anions with smaller energy gaps between highest occupied molecular orbital (HOMO) and LUMO, whereas superoxo-like species are produced by those with larger HOMO–LUMO gaps.^{16,21,22} It was also demonstrated that the activated O₂ on Au clusters can be used in CO oxidation.²¹ This fundamental information will provide a design principle for Au-cluster-based catalysts although it does not directly explained the origin of oxidation catalysis of Au catalysts in the real world^{10–15} due to the significant differences in the environments. Our research aim is to develop oxidation catalysts by taking advantage of the size- and charge-specific reactivity of Au clusters against O₂.^{23,24} We focused

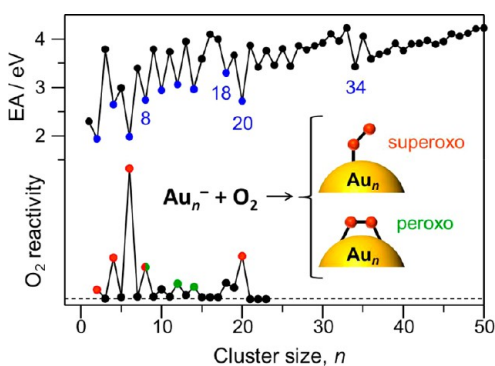


FIGURE 2. Correlation between the electronic structure of the Au clusters and O_2 reactivity.^{16,22}

on aerobic oxidation using O_2 as an oxidant for the development of an environmentally friendly process. The main aim of this Account is not to present a comprehensive survey of the present status of Au catalysts^{10–15} but rather to describe our efforts toward a precise synthesis and detailed characterization of Au clusters and their catalytic applications in aerobic oxidation.

Polymer-Stabilized Gold Cluster Catalysts

We began by preparing small ($d < 2$ nm), nearly free-standing Au clusters to test the hypothesis that small Au clusters in the real world will also show size-specific oxidation catalysis. To minimize the environmental effects, Au clusters were weakly stabilized by a water-soluble polymer, polyvinylpyrrolidone (PVP),^{25,26} conventionally used in the stabilization of colloidal metal NPs.²⁷ Importantly, part of the Au cluster surface stabilized with PVP is exposed to small molecules and metal ions, which enables catalytic conversion of substrates and seed-mediated growth of the Au clusters.²⁸ In the following, we describe the controlled synthesis and size-dependent oxidation catalysis of PVP-stabilized Au clusters (Au:PVP) for aerobic alcohol oxidation and compare the reaction mechanisms of free Au clusters and Au:PVP.

Synthesis and Characterization. To synthesize small Au clusters, the growth of the nucleus should be kinetically terminated at an early stage by increasing the relative concentration of PVP and using a strong reducing reagent ($NaBH_4$, etc.) to facilitate instantaneous reduction of all the Au ions. In our original method, two aqueous solutions of $AuCl_4^-$ and BH_4^- placed in conventional reservoirs were mixed to obtain a brownish hydrosol (batch mixing).²⁵ Transmission electron microscopy (TEM) analysis, powder X-ray diffraction (XRD), and optical spectroscopy showed that small ($d < 2$ nm) Au clusters with a narrow diameter

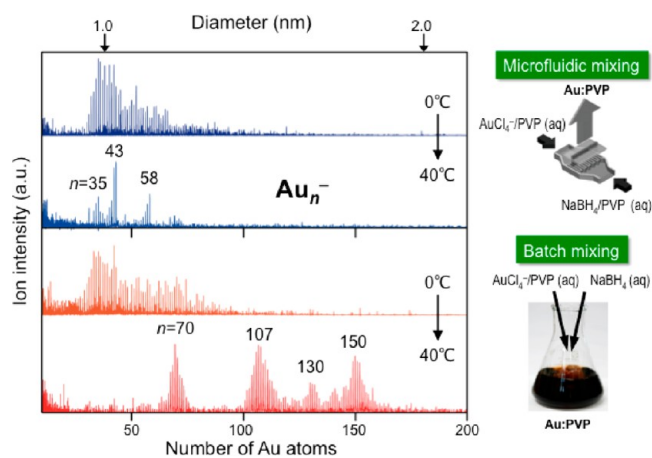


FIGURE 3. Negative-ion MALDI mass spectra of Au:PVP prepared by microfluidic (top) and batch mixing (bottom) at different temperatures. Adapted with permission from ref 30. Copyright 2009 American Chemical Society.

distribution were formed. However, we cannot further narrow the diameter distribution if batch mixing is employed. One of the major reasons for the polydispersity is the inhomogeneous mixing of $AuCl_4^-$ and BH_4^- because the reduction proceeds instantaneously. We previously demonstrated that the diameter distribution can be improved remarkably by homogeneous mixing using a microfluidic mixer.²⁹ In the microfluidic mixer, the two solutions are laminated into thin substreams (70 μm in the case of SIMM-V2, Institute für Mikrotechnik Mainz GmbH) and overlaid (Figure 3). TEM and powder XRD analysis indicated the improvement in the size distribution with the average diameter decreasing to 1.1 nm.

We employed matrix-assisted laser desorption/ionization (MALDI) mass spectrometry to gain further insight into the size distribution of Au:PVP at atomic resolution.³⁰ Figure 3 shows typical negative-ion MALDI mass spectra of Au:PVP prepared by batch and microfluidic methods at different temperatures. The Au clusters in PVP could be desorbed in the form of Au_n^- . Close inspection of the size distributions of Au:PVP prepared at 0 °C reveals that microfluidic mixing yields slightly smaller clusters than batch mixing (Figure 3), which is consistent with the results of the TEM and XRD measurements. We discovered that the populations of Au clusters with sizes of 35, 43, 58, 70, 107, 130, and 150 became prominent when the temperature was increased (Figure 3).³⁰ There is also a notable difference in the temperature dependence of the two mixing modes; the average size did not change appreciably in microfluidic mixing, but it increased significantly in batch mixing. This suggests that microfluidic mixing is a promising method for

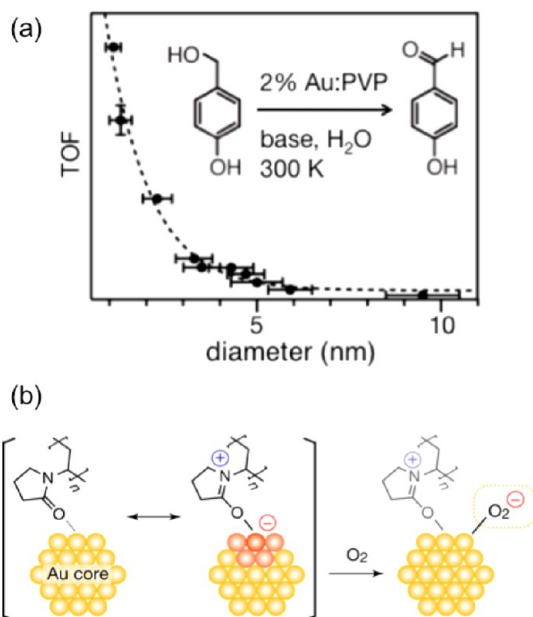


FIGURE 4. (a) Dependence of the catalytic activity on the Au:PVP size for the oxidation of 4-(hydroxymethyl)phenol. (b) Proposed mechanism for activation of O₂ by Au:PVP. Adapted with permission from ref 31. Copyright 2009 American Chemical Society.

(Figure 4b).³¹ The β -hydrogen of the alkoxide is abstracted by an O₂ anionic species thus activated on the Au clusters. In support of this mechanism, the catalytic activity of Au:PVP was further enhanced by Ag doping ($\leq 5\%$), which resulted in an increase in the electronic charge supplied to the Au site by the intracluster electron transfer from the Ag dopant.³³ Recently, the enhanced catalytic activity of AuPd:PVP for the aerobic oxidation of glucose and 1-phenylethanol was also explained in terms of electron transfer from Pd to Au within AuPd NPs (2–3 nm).^{36,37} The essential role of PVP was demonstrated by the finding that both the electronic charge and the activity of Au clusters (~ 1.4 nm) were reduced when PAA was used as a stabilizer.³¹ These results show that Au clusters are catalytically active for aerobic oxidation when they are sufficiently small and negatively charged, as in the case of Au clusters in the gas phase.²¹ The close similarity in the key step for aerobic oxidation in both bare and PVP-stabilized Au clusters suggests that cluster-based catalysts can be designed and developed under a rational concept.

A different mechanism has been proposed for the involvement of O₂ in aerobic alcohol oxidation catalyzed by a Au catalyst intercalated into a polystyrene-based cross-linked polymer.³⁸ It was suggested that hydrogen or hydride of alcohol is transferred directly to the Au clusters followed by the abstraction of hydrogen by O₂ to form a HOO[•] radical. We believe that the different mechanisms are associated with the difference in the charge states of the Au clusters.

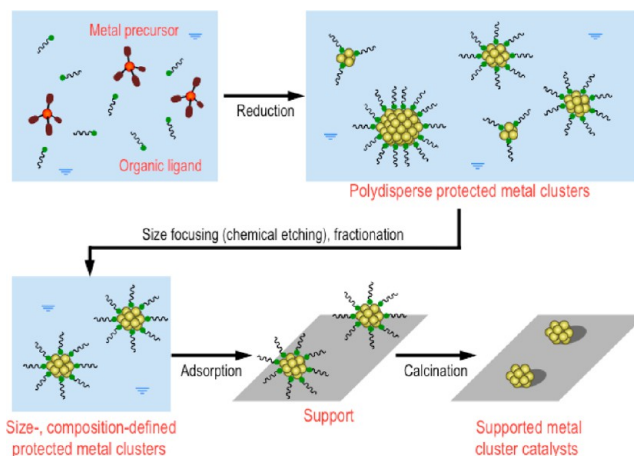


FIGURE 5. Controlled synthesis of supported Au cluster catalysts.

Supported Gold Cluster Catalysts

Supported Au catalysts have several practical benefits such as robustness and ease of reuse as compared with colloidal Au catalysts.^{10–15} However, the conventional method used for supported AuNPs cannot be applied for the precision synthesis of small Au clusters on solid supports. Controlling the size and composition precisely and independently has been a great technical challenge but one that is essential for understanding the effects of the structure on the catalysis. The first aim of our research was to overcome these synthetic problems. We developed a new method using ligand-protected Au clusters with precisely defined sizes and compositions.^{39–42} Our approach is shown schematically in Figure 5. Size- and composition-controlled Au clusters protected by organic ligands such as phosphine (R₃–P) and thiol (R–SH) are prepared^{23,43,44} and a given amount of protected Au clusters are then homogeneously adsorbed on the surface of the solid support in the liquid phase. Removal of the ligands by heat treatment leaves only the Au clusters on the surface. The key to this method is to suppress the aggregation of the resulting Au clusters on the solid surface by decreasing the density of the clusters. In the following, we present examples of the size- and composition-controlled synthesis of supported Au clusters. The second aim of our research was to understand the effect of individual structure parameters such as the size and composition on the oxidation catalysis. We chose chemically inert support materials such as mesoporous silica (SBA-15),³⁹ hydroxyapatite (HAP),^{40,41} and multiwalled carbon nanotubes (CNTs)⁴² to achieve this.

Size-Controlled Synthesis and Characterization. Au clusters protected by phosphines and thiolates are ideal precursors of the size-controlled, supported Au cluster

catalysts because the cluster size can be controlled precisely and systematically.^{23,43,44} Figure 6 plots the chemical compositions of ligand-protected Au clusters that have been isolated so far. Thiolate-protected Au clusters have been studied extensively in the last two decades since the first report by Brust et al.⁴⁵ In 2005, we reported the first size-selective synthesis of $Au_n(SG)_m$ clusters (GSH, glutathione) using polyacrylamide gel electrophoresis.⁴⁶ A series of $Au_n(SR)_m$ clusters with well-defined sizes ($n = 11, 12, 18, 22, 25, 29, 33, 36, 38, 39, 55, 68, 102, 130, 144, 187, \text{ and } 333$) have been isolated so far.^{23,43,44} Single-crystal XRD studies revealed that these clusters are composed of a highly symmetrical core and Au–SR interfacial oligomers (the details of the structures are not given here because this is outside the scope of the present Account). Recently, we reported Au clusters protected by alkynes, $Au_{34}(PA)_{16}$, $Au_{54}(PA)_{26}$, etc. (PA, $PhC\equiv C-$), which have a new ligand binding motif.^{47,48} Since the number of well-defined, protected Au clusters has been increasing rapidly, there are now a wide variety of clusters that can be used as precursors for size-selected supported Au clusters.

Although catalysis was observed with ligand-protected Au clusters by Li and Jin,⁴⁹ we found that the catalytic activity is significantly enhanced when the ligands are removed and a larger surface area is exposed. Several reports of size-controlled Au clusters using this approach have recently been published. For example, we synthesized Au_{11} within mesoporous SBA-15 by the calcination of $[Au_{11}(PPh_3)_8Cl_2]^+$ at 200 °C. The large surface area of SBA-15 (specific surface area $\sim 900 \text{ m}^2/\text{g}$) enables Au_{11} clusters to be deposited on the support with a high dispersion, and the cluster size did not change during the ligand removal (Figures 7a,b).³⁹ In addition, we synthesized for the first time a series of Au_n ($n = 10, 18, 25, \text{ and } 39$) on HAP using $Au_n(SG)_m$ as a starting material (Figures 7c–f).⁴¹ High-angle annular dark field (HAADF) aberration-corrected scanning transmission electron microscopy (STEM) images indicated that the cluster size did not change during the calcination process, although aggregation of the clusters via diffusion was observed at high loadings.⁵⁰ Turner et al.⁵¹ and Ma et al.⁵² reported the production of Au_{55}/SiO_2 and $Au_{144}/CuO/\text{mesoporous silica}$, respectively, by removing the ligands from the corresponding protected Au clusters with a thermal treatment. In all those cases, the geometrical structures of the Au clusters changed considerably as a result of ligand desorption and by interaction with the support surface. In this regard, these structures are not uniform even though the size is uniform.

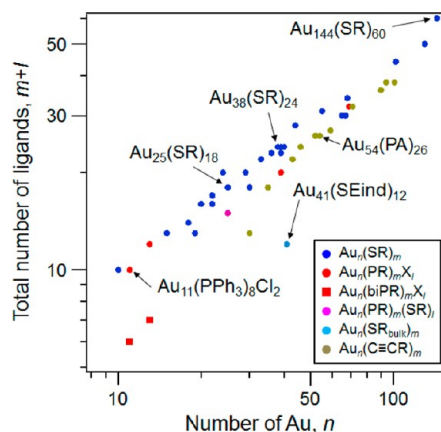


FIGURE 6. Plot of the chemical compositions of ligand-protected Au clusters.

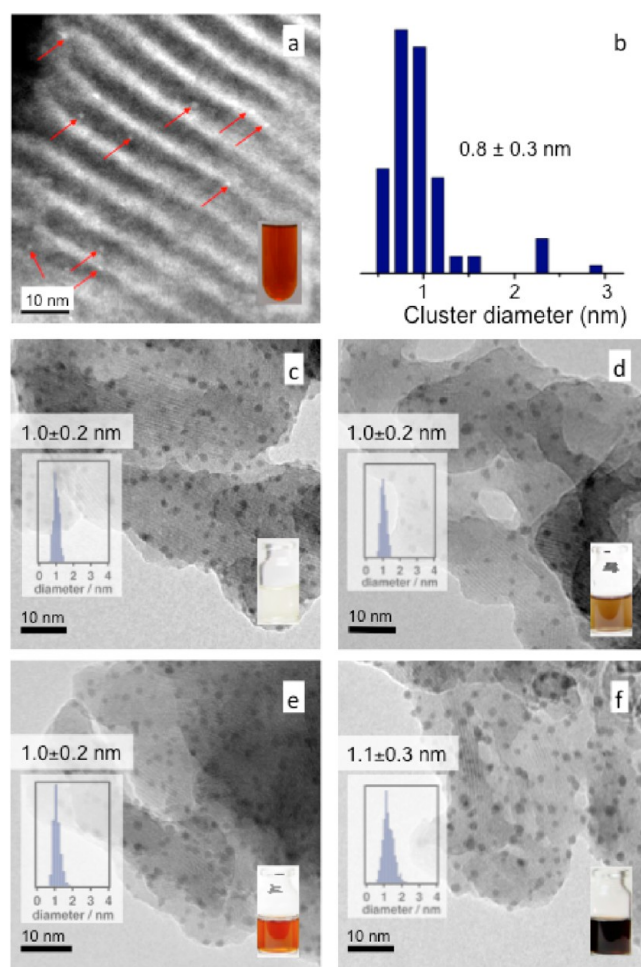


FIGURE 7. (a) HAADF-STEM image and (b) size distribution of Au_{11}/SBA .³⁹ TEM images and size distributions of Au_n/HAP with $n =$ (c) 10, (d) 18, (e) 25, and (f) 39.⁴¹ The images shown in the insets indicate the dispersions of the original protected Au clusters. Adapted with permission from refs 39 and 41. Copyright 2009 and 2011 American Chemical Society.

Composition-Controlled Synthesis and Characterization. Recently, ligand-protected bimetallic clusters such as

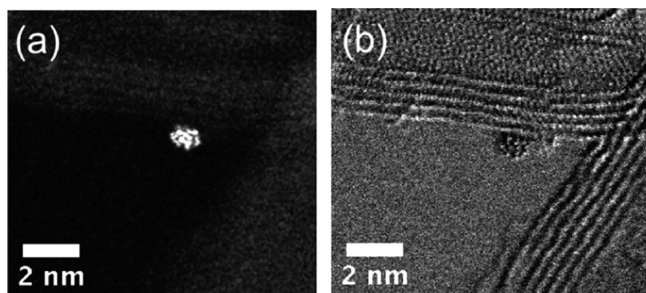


FIGURE 8. (a) Dark-field and (b) bright-field images of PdAu₂₄/CNT. From ref 55. Reproduced by permission of The Royal Society of Chemistry.

Pd₁Au₁₀(PPh₃)₈Cl₂, Pt₁Au₂₄(SR)₁₈, Pd₁Au₂₄(SR)₁₈, Ag_xAu_{25-x}(SR)₁₈ (1 ≤ x ≤ 11), Cu_xAu_{25-x}(SR)₁₈ (1 ≤ x ≤ 5), Pd₂Au₃₆(SR)₂₄, Ag_xAu_{38-x}(SR)₂₄ (1 ≤ x ≤ 10), and Ag_xAu_{144-x}(SR)₆₀ (30 ≤ x ≤ 54) have been synthesized.^{44,53,54} Interestingly, these bimetallic clusters have counterparts in pure Au clusters: Au₁₁(PPh₃)₈Cl₂, Au₂₅(SR)₁₈, Au₃₈(SR)₂₄, and Au₁₄₄(SR)₆₀. Thus, only the composition of bimetallic cluster catalysts on supports can be varied while keeping the total number of atoms constant by the method outlined in Figure 5 using the bimetallic clusters listed above.

We recently synthesized Au₂₅ and Pd₁Au₂₄ on CNTs by the calcination of Au₂₅(SC₁₂H₂₅)₁₈ and Pd₁Au₂₄(SC₁₂H₂₅)₁₈ at 450 °C in vacuum.⁴² The removal of the ligands in the form of thiols and disulfide was confirmed by a mass analysis of the desorbed species during the calcination. Aberration-corrected HAADF-STEM observations revealed that the cluster size after calcination was 25 ± 2, which is in agreement with the Pd₁Au₂₄(SC₁₂H₂₅)₁₈ precursor (Figure 8).⁵⁵ Preliminary EXAFS analysis of Pd₁Au₂₄/CNTs suggests that the Pd atom is located between the Au cluster and the CNT, whereas it was located at the center of the icosahedral Pd@Au₁₂ core in the Pd₁Au₂₄(SC₁₂H₂₅)₁₈ precursor.⁵⁶

Oxidation Catalysis. Supported Au cluster catalysts were successful in catalyzing various types of oxidation reactions, as shown in Scheme 2, including oxidation of primary and secondary alcohols,^{39,42} alkenes (C=C bonds),⁴⁰ and alkanes (C-H bonds).⁴¹ For example, we have reported that Au₁₁ (*d* = 0.8 nm)/SBA-15 catalyzed oxidations of primary and secondary alcohols using hydrogen peroxide as an oxidant under microwave irradiation.³⁹ Epoxidation of styrene to styrene oxide proceeded with a high selectivity (92%) over supported Au₂₅ immobilized on HAP;⁴⁰ the styrene oxide selectivity of Au₂₅/HAP was much higher than that of Au (*d* ≈ 1.8 nm)/HAP prepared by the conventional method and is a result of the reduction in the decomposition rate of the generated styrene oxide as the Au cluster size is reduced.

SCHEME 2. Oxidation Reactions Catalyzed by Supported Au Clusters

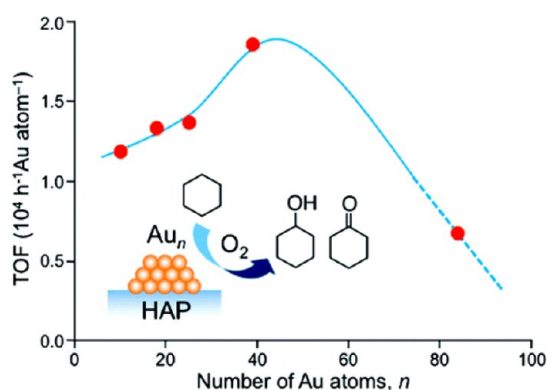
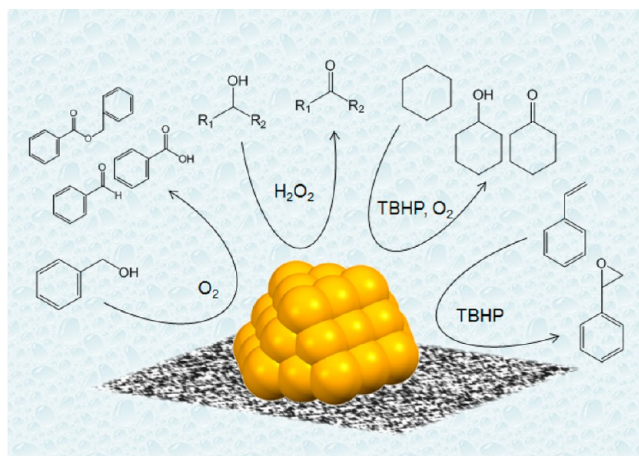


FIGURE 9. Size dependence of Au_{*n*}/HAP on the catalytic activity for cyclohexane oxidation.⁴¹ Adapted with permission from ref 41. Copyright 2011 American Chemical Society.

We also investigated the effect of the size of Au clusters supported on HAP on the catalytic activity for the cyclohexane oxidation reaction.⁴¹ All the Au_{*n*} clusters (*n* = 10, 18, 25, 39, and ~85) on HAP converted cyclohexane selectively into cyclohexanol and cyclohexanone, which are important intermediates of nylon-related materials. Figure 9 shows the size dependence of the TOF of cyclohexane oxidation over Au_{*n*}/HAP. Volcano-like behavior was observed, with the TOF peaking at Au₃₉. Figure 9 illustrates that the effect of cluster size is not obscured by the heterogeneity of the cluster geometry. The size dependence in Figure 9 cannot be explained merely by geometrical factors such as surface area and the number of low-coordination sites. However, both the nature of reactive species and the reaction mechanism are still unclear. In contrast to the case of Au:PVP, small cationic Au clusters can be active as pointed out by Gates and Hutchings.^{10,13}

Very recently, we studied the effect of a single Pd dopant atom on the catalysis of Au₂₅ clusters for benzyl alcohol

oxidation using Au₂₅/CNT and Pd₁Au₂₄/CNT catalysts.⁴² We found that the catalytic activity of Pd₁Au₂₄/CNT was much higher than that of Au₂₅/CNT. This constituted the first demonstration of the effects of single-atom doping on catalysis. DFT calculations of bare Au₂₅ and Pd₁Au₂₄ revealed that the Pd dopant atom prefers to be located inside the shell of Au atoms and donates an electron to neighboring Au atoms.⁵⁵ Such intracluster electron transfer may activate the Au atoms and enhance the catalytic activity of benzyl alcohol oxidation.

Conclusions

This Account has focused on our efforts to achieve precision synthesis of small (<2 nm) Au clusters, stabilized by polymers and immobilized on supports, for various catalytic applications. Chemically inert materials were selected for the stabilizers and supports to develop Au cluster catalysts by taking full advantage of their intrinsic size-specific chemical nature. To test the possibility that the intrinsic chemical reactivity of bare Au clusters to O₂ can be translated into aerobic oxidation catalysis in the real world, the Au clusters were weakly stabilized with PVP while exposing part of the surface for catalysis. The cluster size was controlled precisely by homogeneous and rapid mixing of Au³⁺ precursor ions with NaBH₄ in a micromixer. MALDI mass spectrometry of the resulting Au:PVP indicated the presence of magic numbers in the size distribution, which are similar to those of the bare clusters. We found that only Au clusters smaller than a certain critical size show aerobic oxidation and concluded that the catalysis is associated with the unique electronic structure of the small Au clusters. In contrast to PVP-stabilized Au clusters, Au cluster catalysts immobilized on solid supports have several practical benefits. We developed a reproducible method to precisely control the size and composition of supported Au clusters using ligand-protected Au and Au-based bimetallic clusters. Aberration-corrected HAADF-STEM allowed us to count the number of atoms contained in individual clusters based on the image contrast. We also demonstrated that there is an optimal Au cluster size on HAP for the efficient oxidation of cyclohexane, and a single Pd dopant atom in a Au₂₅ cluster greatly improves the activity of aerobic oxidation of benzyl alcohol. The nonscalable chemistry that we have demonstrated here for Au clusters can be bedrock for the development of novel catalysts using nonprecious metals.

BIOGRAPHICAL INFORMATION

Seiji Yamazoe received his Ph.D. degree in chemistry from Kyoto University in 2008 under the supervision of Prof. Tsunehiro Tanaka.

He then moved to the Department of Materials Chemistry, Ryukoku University, in 2008 as an assistant professor. Since 2012, he has been working at the Department of Chemistry, The University of Tokyo, as an assistant professor. His current research interests include structural analysis of metal clusters using synchrotron radiation and catalyst development using these metal clusters.

Kiichirou Koyasu received his Ph.D. degree in chemistry in 2006 from Keio University under the supervision of Prof. Atsushi Nakajima. He then worked with Prof. G. Ganteför at the University of Konstanz, Germany, as a postdoctoral fellow until 2008 and joined the group of Prof. Seki at Nagoya University as a postdoctoral researcher. In 2009, he was appointed as an assistant professor in the Department of Chemistry at Keio University before moving to the Department of Chemistry at Tohoku University. He has been an associate professor at the Department of Chemistry, The University of Tokyo, since 2013. His current research is focused on investigating correlations between electronic structures of free metal clusters and their chemical reactions in the gas phase.

Tatsuya Tsukuda received his Ph.D. degree in chemistry in 1994 from the University of Tokyo, supervised by Prof. Tamotsu Kondow. After completing postdoctoral research under the guidance of Prof. Kondow at RIKEN, he was appointed as an assistant professor in the Department of Basic Sciences at the University of Tokyo in 1994. He was then appointed as an associate professor at the Institute for Molecular Science in 2000 and promoted to the position of professor at the Catalysis Research Center of Hokkaido University in 2007. He has been a professor at the Department of Chemistry, The University of Tokyo, since 2011. His research interests lie in the field of size-selected synthesis of metal clusters protected by ligands and supported on solid materials and their related catalytic applications.

FOOTNOTES

*Corresponding author. E-mail: tsukuda@chem.s.u-tokyo.ac.jp. The authors declare no competing financial interest.

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