

CATALYTIC CHEMISTRY

Annual Research Highlights

(1) “Aerobic oxidation of cyclohexane catalyzed by size-controlled Au clusters on hydroxyapatite”

In this work, we synthesized gold clusters, Au_n ($n = 10, 18, 25, 39$), with atomically-controlled sizes on hydroxyapatite (HAP) and studied the catalysis for aerobic oxidation of cyclohexane. These Au_n /HAP catalysts could efficiently oxidize cyclohexane to cyclohexanol and cyclohexanone. The turnover frequency monotonically increased with an increase in the size, reaching values as high as $18500 \text{ h}^{-1} \text{ Au atom}^{-1}$ at $n = 39$, and thereafter decreased with a further increase in n up to $n \sim 85$. This finding provides a fundamental insight into size-specific catalysis of gold in the cluster regime (diameter $< 2 \text{ nm}$) and a guiding principle for rational design of Au cluster-based catalysts.

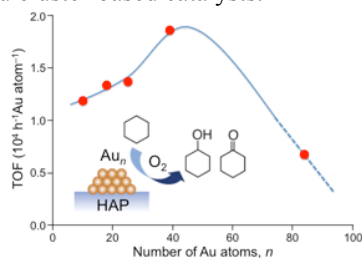
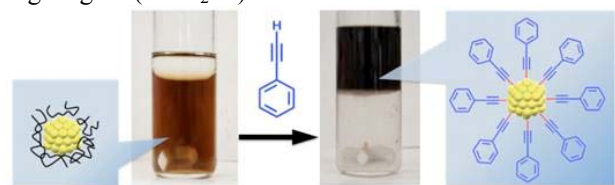


Fig. 1 TOF values as a function of the cluster size of Au_n /HAP 1.(1)-1) *ACS Catal.*, **1**, 2-6 (2011).

(2) “Organogold clusters protected by phenylacetylene”

A new class of monolayer-protected Au clusters with Au-C covalent bonds (organogold clusters) was synthesized by ligating phenylacetylene (PhC≡CH) to PVP-stabilized Au clusters. Matrix-assisted laser desorption/ionization mass spectrometry revealed for the first time a series of stable compositions of the organogold ($Au:C_2Ph$) clusters.



PVP-stabilized Au clusters PA-protected organogold clusters 1.(1)-7) *J. Am. Chem. Soc.*, **133**, 20123-20125 (2011).

(3) “Synthesis and characterization of $Au_{102}(p\text{-MBA})_{44}$ ”

The synthesis of $Au_{102}(p\text{-MBA})_{44}$ on a preparative scale in high yield is described. Various analytical methods are shown to give results consistent with the composition and known structure of the particles, showing the preparation is essentially homogeneous, and attesting to the validity of the methods as well.

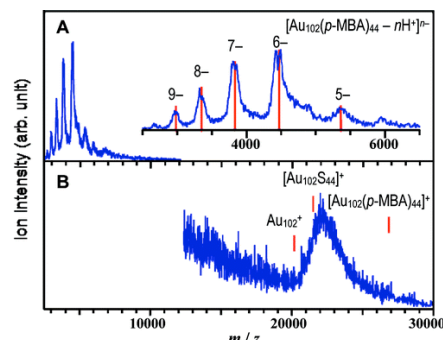


Fig. 2 (A) ESI and (B) LDI mass spectra of $Au_{102}(p\text{-MBA})_{44}$ 1. (1)-3) *J. Am. Chem. Soc.*, **133**, 2976-2982 (2011).

(4) “Isolation and structural characterization of magic silver clusters protected by 4-(tert-butyl)benzyl mercaptan”

Small silver clusters (average diameter of 1.2 nm) protected by 4-(tert-butyl)benzyl mercaptan (BBSH) were converted to stable, monodisperse clusters (2.1 nm) by a ripening process with excess amount of BBSH. Multiple characterizations of the isolated magic clusters revealed an approximate chemical composition of $Ag_{-280}(SBB)_{-120}$.

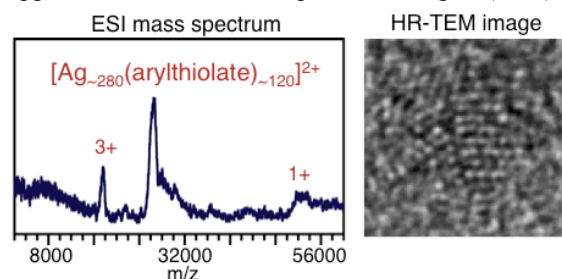


Fig. 3 ESI mass spectrum (left) and high resolution TEM image (right) of $Ag_{-280}(SBB)_{-120}$ 1.(1)-5) *Chem. Commun.*, **47**, 5693-5695 (2011).

(5) “ ^{197}Au Mössbauer spectroscopy of $Au_{25}(\text{SG})_{18}$ ”

Reanalysis of the ^{197}Au Mössbauer spectrum of $Au_{25}(\text{SG})_{18}$ (SG = glutathionate) based on the structure determined by single crystal XRD analysis gave a reasonable fit, demonstrating that ^{197}Au Mössbauer spectroscopy is a powerful tool for predicting the structural motifs of thiolate-protected Au clusters.

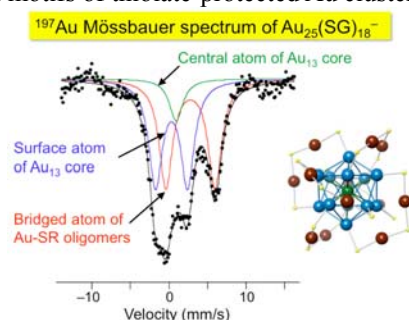


Fig. 4 ^{197}Au Mössbauer spectrum (left) and geometrical structure (right) of $Au_{25}(\text{SG})_{18}$ 1.(1)-6) *Chem. Lett.*, **40**, 1292-1293 (2011).

研究ハイライト

(1) ハイドロキシアパタイト担持金クラスターのサイズ選択的合成と酸化触媒としての応用

水溶性チオールグルタチオンで保護された金クラスター Au_n ($n = 10, 18, 25, 39$) をハイドロキシアパタイト (HAP) に吸着させた後に焼成することによって、サイズ制御された担持金クラスター触媒を系統的に合成した。得られた金クラスターは、シクロヘキサンの空気酸化反応に対して高い触媒活性を示すことを見いだした ($18500 \text{ h}^{-1} \text{ Au atom}^{-1}$ at $n = 39$)。サイズ効果を調べたところ、39 量体が最も高い活性を示した。

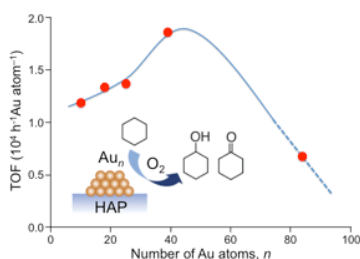
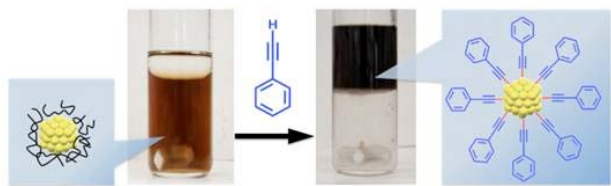


図1 Au_n /HAP のシクロヘキサン酸化に対する触媒活性とサイズの関係

1.(1)-1) *ACS Catal.*, **1**, 2-6 (2011).

(2) Organogold cluster : 金-炭素結合による金クラスターの安定化

ポリビニルピロリドン (PVP) で安定化された金クラスターをフェニルアセチレン ($\text{PhC}\equiv\text{CH}$) と反応させることで、金-炭素共有結合によって安定化された新しい単分子保護金クラスター (organogold clusters) を合成した。マトリックス支援脱離イオン化質量分析法によって安定組成の系列を見いだした。



PVP-stabilized Au clusters PA-protected organogold clusters
1.(1)-7) *J. Am. Chem. Soc.*, **133**, 20123-20125 (2011).

(3) $Au_{102}(p\text{-MBA})_{44}$ の合成と評価

p -メルカプト安息香酸 (p -MBA) で保護された金 102 量体を合成し、電子顕微鏡、質量分析、粉末 X 線回折、熱重量分析法などを用いて評価した。

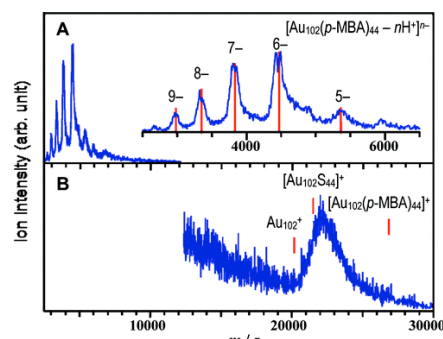


図2 $Au_{102}(p\text{-MBA})_{44}$ の(A)ESI, および(B)LDI 質量スペクトル。

1. (1)-3) *J. Am. Chem. Soc.*, **133**, 2976-2982 (2011).

(4) チオール保護銀クラスターの合成と評価

バルキーなチオール (SBB) で保護した銀クラスターを合成し、電子顕微鏡、質量分析、粉末 X 線回折、熱重量分析法などを用いて評価した。その結果、組成が $Ag_{-280}(SBB)_{-120}$ で表すことができることを見いだした。

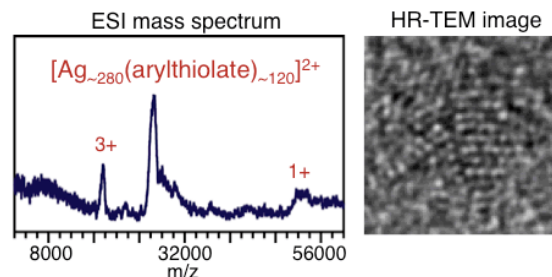


図3 $Ag_{-280}(SBB)_{-120}$ の ESI 質量スペクトル (左), および高分解能電子顕微鏡写真 (右)

1.(1)-5) *Chem. Commun.*, **47**, 5693-5695 (2011).

(5) $Au_{25}(SG)_{18}^-$ の ^{197}Au メスバウワー分光

グルタチオン (GS) で保護された金 25 量体の ^{197}Au メスバウワースペクトルを、単結晶構造解析の結果をもとに再解析した。その結果、化学的な環境の異なる 3 種類の金の存在比を定量的に説明することに成功した。

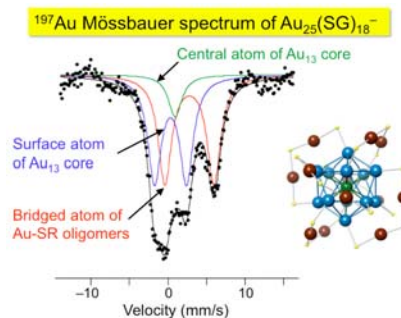


図4 $Au_{25}(SG)_{18}^-$ の ^{197}Au メスバウワースペクトル (左) と幾何構造 (右)

1.(1)-6) *Chem. Lett.*, **40**, 1292-1293 (2011).

1. 原著論文

(1) Refereed Journals

- 1) Y. Liu, H. Tsunoyama, T. Akita, S. Xie and T. Tsukuda, "Aerobic oxidation of cyclohexane catalyzed by size-controlled Au clusters on hydroxyapatite: size effect in the sub-2 nm regime", *ACS Catal.*, **1**, 2-6 (2011).
- 2) M. Yamauchi, R. Abe, T. Tsukuda, K. Kato and M. Takata, "Highly selective ammonia synthesis from nitrate with photocatalytically generated hydrogen on CuPd/TiO₂", *J. Am. Chem. Soc.*, **133**, 1150-1152 (2011).
- 3) Y. Levi-Kalishman, P. D. Jadzinsky, N. Kalisman, H. Tsunoyama, T. Tsukuda, D. A. Bushnell and R. D. Kornberg, "Synthesis and characterization of Au₁₀₂(p-MBA)₄₄ nanoparticles", *J. Am. Chem. Soc.*, **133**, 2976-2982 (2011).
- 4) M. Yamauchi and T. Tsukuda, "Production of ordered (B2) CuPd nanoalloy by low-temperature annealing under hydrogen atmosphere", *Dalton Trans.*, **40**, 4842-4845 (2011).
- 5) Y. Negishi, R. Arai, Y. Niihori and T. Tsukuda, "Isolation and structural characterization of magic silver clusters protected by 4-(*tert*-butyl)benzyl mercaptan", *Chem. Commun.*, **47**, 5693-5695 (2011).
- 6) T. Tsukuda, Y. Negishi, Y. Kobayashi and N. Kojima, "¹⁹⁷Au Mössbauer spectroscopy of Au₂₅(SG)₁₈⁻ revisited", *Chem. Lett.*, **40**, 1292-1293 (2011).
- 7) P. Maity, H. Tsunoyama, M. Yamauchi, S. Xie and T. Tsukuda, "Organogold clusters protected by phenylacetylene", *J. Am. Chem. Soc.*, **133**, 20123-20125 (2011).

2. 総説・解説

- 1) T. Tsukuda, H. Tsunoyama and H. Sakurai, "Aerobic oxidations catalyzed by colloidal nanogold", *Chem. Asian J.*, **6**, 736-748 (2011).
- 2) H. Tsunoyama, Y. Liu, T. Akita, N. Ichikuni, H. Sakurai, S. Xie and T. Tsukuda, "Size-controlled synthesis of gold clusters as efficient catalysts for aerobic oxidation", *Catal. Surv. Asia*, **15**, 230-239 (2011).

3. 著書

- 1) 角山寛規・佃達哉: 「金属ナノクラスターの化学」, 現代化学増刊 44 有機金属化学の最前線-多様な元素を使いこなす- (宮浦憲夫, 鈴木寛治, 小澤文幸, 山本陽介, 永島英夫編, 東京化学同人, 2011) 208-220.