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Efficient and selective epoxidation of styrene with TBHP catalyzed by Au₂₅ clusters on hydroxyapatite[†]

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Au₂₅ clusters supported on hydroxyapatite oxidized styrene in toluene with 100% conversion and 92% selectivity to the epoxide, under optimum conditions and using anhydrous *tert*-butyl hydroperoxide (TBHP) as an oxidant.

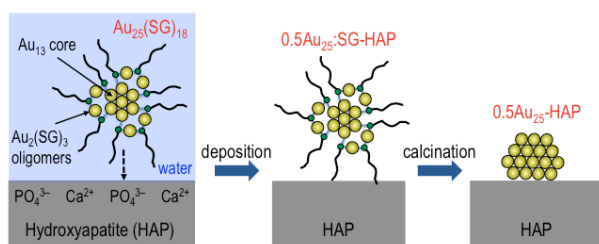
In 1998, Haruta and coworkers demonstrated for the first time that supported Au nanoparticles (AuNPs) are effective for the direct epoxidation of propene using molecular oxygen.¹ Since then, supported gold catalysts have been used for the selective
15 epoxidation/oxidation of various alkenes such as styrene, cyclohexene, *cis*-cyclooctene and *trans*-stilbene.²⁻⁷ A major current challenge is to use O₂ as a green oxidant.^{3,4,5c} Lambert and coworkers have demonstrated that Au₅₅ clusters supported on silica can catalytically activate O₂ for styrene epoxidation
20 because of the electronic structures of the clusters, although the yield of the epoxide is not high (~5%).⁴ This work hints at the possibility that there is an optimal cluster size for the efficient and selective oxidation of alkenes. Here we focus on the epoxidation of styrene and aim to systematically study the
25 effect on the catalytic activity of the size of Au clusters that are immobilized on hydroxyapatite (HAP; Ca₁₀(PO₄)₆(OH)₂).⁸ We use *tert*-butyl hydroperoxide (TBHP) as an oxidant since it is known to be more effective than O₂ for alkene oxidations.⁵⁻⁷ We describe the synthesis of HAP-supported
30 Au₂₅ clusters; they show a higher catalytic performance (100% conversion and 92% selectivity to the epoxide) than larger analogs.

The preparation of HAP-supported Au₂₅ catalysts is depicted in Scheme 1. The basic idea is to use as a precursor
35 ligand-protected Au clusters with a well-defined core size.^{4,9} In brief, we first deposit Au₂₅ clusters protected by 18 glutathionate (GS) ligands, Au₂₅(SG)₁₈, on an HAP support and then calcine the composite to remove the GS ligands.[‡] The Au₂₅(SG)₁₈ cluster is a water-soluble, stable cluster
40 compound that we first identified in 2005.¹⁰ Recent single crystal XRD results on Au₂₅(SC₂H₄Ph)₁₈ revealed that it is composed of an icosahedral Au₁₃ core fully protected by six

55 Au₂(SC₂H₄Ph)₃ oligomers.¹¹ In the present study, HAP was used as a support material for the Au clusters.¹² We expected that Au₂₅(SG)₁₈ could be adsorbed on HAP by electrostatic interaction between Ca²⁺/PO₄³⁻ moieties and the GS ligands, and that HAP could stabilize bare Au₂₅ clusters against
60 sintering due to strong interaction with PO₄³⁻ moiety.¹³

The Au₂₅(SG)₁₈ clusters prepared by the reported procedure¹⁰ and HAP were dispersed in water. The purity of the Au₂₅(SG)₁₈ sample was confirmed by the profile and extinction coefficient of the optical spectrum and
65 thermogravimetric (TG) analysis. After the mixture was stirred for 4 h, the composite of Au₂₅(SG)₁₈ and HAP was collected by filtration. The Au₂₅(SG)₁₈ clusters were found to be adsorbed completely on HAP as evidenced by the colorless filtrate (ESI,† Fig. S1). The Au loading of the composites
70 thus obtained is 0.5 wt% (ESI,† Table S1), so the composite is hereafter referred to as 0.5Au₂₅:SG-HAP. Similar profiles of the optical spectra for Au₂₅(SG)₁₈ and the 0.5Au₂₅:SG-HAP composite (ESI,† Fig. S2) indicate that Au₂₅(SG)₁₈ is adsorbed intact on the HAP surface (Scheme 1). High-angle
75 annular dark-field scanning transmission electron microscopy (HAADF-STEM) confirmed that monodisperse Au clusters with an average diameter of 1.0 ± 0.4 nm are distributed in the 0.5Au₂₅:SG-HAP composite (ESI,† Fig. S3). The diameter of the Au core is comparable to that of Au₂₅ (~0.9 nm), assuming
80 a spherical shape.

The 0.5Au₂₅:SG-HAP composite was then incubated for removal of the thiolate ligands. The results of thermogravimetric analysis revealed a 49% weight loss of Au₂₅(SG)₁₈ after calcination at 300 °C *in vacuo* for 2 h (ESI,†
85 Fig. S4); this weight corresponded to the calculated weight of the GS ligands in Au₂₅(SG)₁₈ (53%). Thus, 0.5Au₂₅:SG-HAP was calcined under the above mentioned conditions to remove the GS ligands. This removal was confirmed by inductively coupled plasma (ICP) measurements. After calcination, the
90 sulfur content reduced from 0.058 wt% to 0.005 wt%, which was comparable to the amount of sulfur impurity in HAP. An HAADF-STEM image of the resulting Au₂₅-HAP shows that most of the clusters are 1.2-1.5 nm in size (Fig. 1A). Fig. 1B represents a histogram of the Au cluster size determined by
95 measuring more than 400 particles. The average diameter is determined to be 1.4 ± 0.6 nm, larger than that for 0.5Au₂₅:SG-HAP (ESI,† Fig. S3). Close inspection of Fig. 1A reveals Au clusters with non-spherical morphology. Possible explanations for these observations are that (1) larger clusters
100 form because of sintering, or (2) Au₂₅ clusters with various morphologies are formed in the heat-induced structural



Scheme 1. Synthetic procedure of HAP-supported Au₂₅ clusters.

arrangement and because of the strong interaction between Au₂₅ and HAP. We believe that (2) is the correct explanation since the cluster diameter does not change appreciably even when the loading of Au₂₅(SG)₁₈ is reduced to 0.2 wt%.

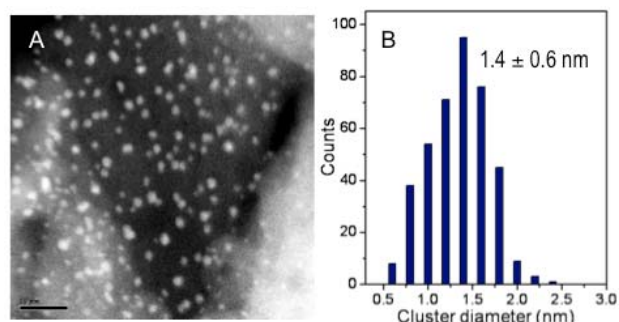


Fig. 1 (A) Representative HAADF-STEM image of 0.5Au₂₅-HAP and (B) size distribution of the Au clusters. The bar in panel (A) represents 10 nm.

For comparison, other 0.5Au-HAP samples were prepared using HAuCl₄ as the precursor by the conventional method such as impregnation (IP), deposition precipitation (DP), and adsorption (Ad) (ESI†). These samples are denoted as 0.5Au-HAP(IP), 0.5Au-HAP(DP) and 0.5Au-HAP(Ad), respectively. Gold contents were confirmed by ICP measurement (ESI,† Table S1). Their Au particle sizes were measured by conventional TEM. The average diameters for 0.5Au-HAP(Ad) and 0.5Au-HAP(IP) were determined to be 1.7 ± 1.2 and 6.0 ± 3.7 nm, respectively, whereas the Au clusters for 0.5Au-HAP(DP) were polydisperse with sizes in the range of 1–20 nm (ESI,† Fig. S5).

The Au-HAP catalysts were also characterized by UV-vis diffuse reflectance spectroscopy. Fig. 2 compares the optical spectra of the four Au-HAP catalysts. The sharp peaks associated with quantized electronic structures of Au₂₅(GS)₁₈ on HAP (ESI,† Fig. S1) are smeared out after calcination (curve a). This change is consistent with the generation of structural isomers of Au₂₅ during calcination and/or by interaction between Au₂₅ and the HAP support. The surface plasmon (SP) band is absent in 0.5Au₂₅-HAP (curve a), whereas it is apparent for 0.5Au-HAP(Ad), 0.5Au-HAP(IP), and 0.5Au-HAP(DP) (curves b-d). This observation indicates that the Au clusters in 0.5Au₂₅-HAP are smaller than those in the other samples. Given that optical spectroscopy probes the

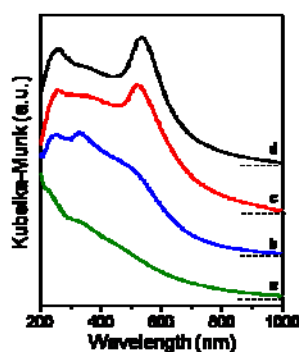


Fig. 2 Diffuse reflectance UV-vis spectra of a) 0.5Au₂₅-HAP, b) 0.5Au-HAP(Ad), c) 0.5Au-HAP(IP), and d) 0.5Au-HAP(DP).

electronic structure of the ensemble of Au clusters and is highly sensitive to the presence of AuNPs (>2 nm), curve a in Fig. 2 indicates that the population of Au clusters larger than 2 nm is negligibly small. These inferences are in consistent with the HAADF-STEM results (Fig. 1B). The BET surface areas of the Au-HAP catalysts were ~30 m²/g (ESI,† Table S1).

To reveal the effect on the catalytic activity of the size of Au clusters, the catalytic performance of monodisperse Au catalysts 0.5Au₂₅-HAP, 0.5Au-HAP(Ad) and 0.5Au-HAP(IP) was compared. Oxidation of styrene (**1**) in toluene at 80 °C using anhydrous TBHP as an oxidant yielded styrene oxide (**2**) as a major product in every case, whereas acetophenone (**3**), benzaldehyde (**4**), benzylalcohol (**5**), and benzoic acid (**6**) were also produced.^{‡14} It was essential to use toluene as a solvent to obtain **2** in a high yield, in sharp contrast to the case of Au/graphite³ and Au/SiO₂.⁴ The use of anhydrous toluene and TBHP was also important for enhancing the yield of **2**. Compounds **3–6** were produced by the oxidation of **1** as well as the toluene solvent; for example, the yields of **4–6** by 0.5Au₂₅-HAP exceed 100% with respect to **1** (ESI,† Fig. S7). For simplicity, we focus here on the conversion of **1** to **2**.

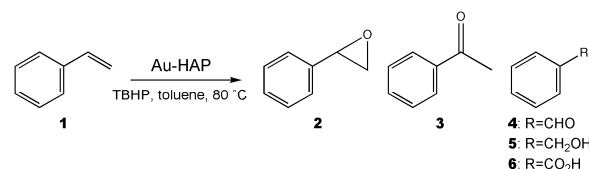


Fig. 3A shows the time evolution of the conversion of **1**, estimated from the GC yield of **1**. The rate constants of the conversion are estimated by assuming first-order kinetics with respect to the substrate (**1**) (ESI,† Fig. S8, Table S2). The rate of conversion for 0.5Au₂₅-HAP is comparable to that of 0.5Au-HAP(Ad), but slightly larger than that of 0.5Au-HAP(IP). However, the conversion reaches >90% for all the catalysts after >12 h. These results suggest that Au clusters on HAP can effectively oxidize **1** regardless of the size. The selectivity of the Au-HAP catalysts toward **2** was calculated using the equation 100 × Y₂/(100 – Y₁), where Y₁ and Y₂ represent the GC yields (in %) of **1** and **2**, respectively. The selectivity of **2** thus estimated is plotted in Fig. 3B as a function of the reaction time. Interestingly, the selectivity of 0.5Au₂₅-HAP (92–95%) is much higher than those (50–60%) of 0.5Au-HAP(Ad) and 0.5Au-HAP(IP). The remarkable difference in the selectivity between 0.5Au₂₅-HAP and 0.5Au-

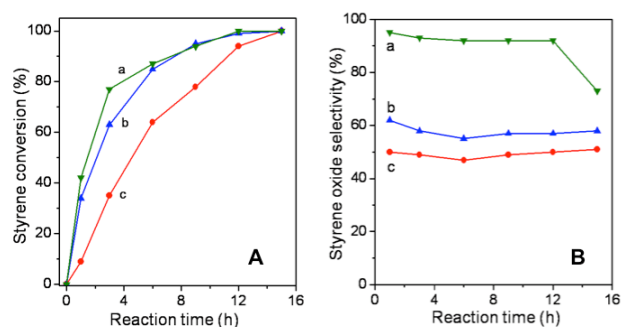


Fig. 3 Time evolution of (A) conversion of **1** and (B) selectivity of **2** for a) 0.5Au₂₅-HAP, b) 0.5Au-HAP(Ad), and c) 0.5Au-HAP(IP).

HAP(Ad) may reflect the difference in geometrical (Fig. 1A) and/or electronic structures (Fig. 2) of the Au clusters although their average diameters appeared to be similar by TEM observation. Because of the high selectivity, the 0.5Au₂₅-HAP catalyst gave the highest yield of **2**, reaching 92% at 12 h.¹⁵ To our knowledge, this yield of styrene oxide is one of the highest reported so far.²⁻⁷ Very recently, AuNPs (3 nm) stabilized by an oligomer of ionic liquid exhibited a styrene conversion of 100% with a selectivity to styrene oxide of 90%, but they were gradually deactivated during the reuse process.^{7b}

What is the reason for the high selectivity of 0.5Au₂₅-HAP?

To answer this question, we compared the rate constant for the decomposition of **2** by the three Au-HAP catalysts in methylcyclohexane. The smallest 0.5Au₂₅-HAP showed the poorest conversion (<15%) while the largest, Au-HAP(IP), showed the highest activity (ESI,† Fig. S9). On the basis of this size effect, we suggest that the high selectivity of 0.5Au₂₅-HAP can be explained on the basis of the extremely slow decomposition of **2** by Au₂₅ clusters. The 0.5Au₂₅-HAP also showed excellent reusability without any significant loss in either the catalytic activity or the selectivity of the formation of **2** (ESI,† Fig. S10). Finally, we tested the catalytic activity of 0.5Au₂₅-HAP against styrene oxidation in toluene in an O₂ atmosphere (1 atm). Microwave heating at 100 °C for 2 h yields **2** with a conversion of 22% and a selectivity of 36 % (ESI,† Table S3), although the reaction conditions were not optimized.

In summary, we developed a reproducible method¹⁶ to immobilize Au₂₅ clusters on HAP using Au₂₅(SG)₁₈ as a precursor. The size of the HAP-supported Au clusters after calcination appeared to be ~1.4 nm by HAADF-STEM observation, slightly larger than that expected for Au₂₅ (~0.9 nm) with a spherical morphology. The Au₂₅ clusters anchored on HAP exhibited higher catalytic performance than larger clusters in the epoxidation of styrene using TBHP as an oxidant. This catalyst could be reused without significant loss of either activity or selectivity. These observations suggest that small Au clusters on HAP is a promising catalyst for the selective epoxidation of alkenes.

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Notes and references

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† Electronic Supplementary Information (ESI) available: optical spectra of Au₂₅(SG)₁₈ in water and on HAP, preparation and characterization TEM images of Au-HAP catalysts, kinetic analysis, result of reuse test. See DOI: 10.1039/b000000x/

‡ Preparation of Catalysts: The Au₂₅(SG)₁₈ precursors were first prepared by following the procedure we reported previously.¹⁰ The Au₂₅(SG)₁₈ clusters (10.7 mg) and HAP (Sigma Aldrich, 1 g) were then dispersed in water and the mixture was stirred for 4 h. The composite of Au₂₅(SG)₁₈

and HAP was collected by filtration and then incubated in vacuo at 300 °C for 2 h.

Catalytic Test: Typically, 50 mg of the Au-HAP catalyst was added to the toluene (10 mL) solution in a test tube (l=30 mm) containing 40 mg of styrene and 200 mg of TBHP. The mixture was stirred at a rate of 1200 rpm while the temperature was kept at 80 °C. The products were extracted and identified by gas chromatography (Shimadzu GC-2014) using authentic samples. The yield of product was determined by gas chromatography using the external standard method.

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- 14 The catalytic activity of HAP is negligibly small; the yield of **2** was <5% after 16 h (ESI,† Fig. S6).
- 15 The decrease in the selectivity when reaction time is >12 h was due to the decomposition of **2** into **3** and **4** (ESI,† Fig. S7).
- 16 Lot-to-lot reproducibility of Au₂₅-HAP was confirmed by UV-vis spectroscopy and measurement of the catalytic activity for styrene oxidation. The spectra of the three independently synthesized Au₂₅-HAP catalysts were nearly identical. Further, the conversion of **1** observed with each of the catalysts was similar with a typical standard deviation of <5%.



Au₂₅ clusters supported on hydroxyapatite oxidized styrene in toluene with 100% conversion and 92% selectivity to the epoxide, under optimum conditions and using anhydrous *tert*-butyl hydroperoxide (TBHP) as an oxidant.