

# Aerobic Oxidation of Cyclohexane Catalyzed by Size-Controlled Au Clusters on Hydroxyapatite: Size Effect in the Sub-2 nm Regime

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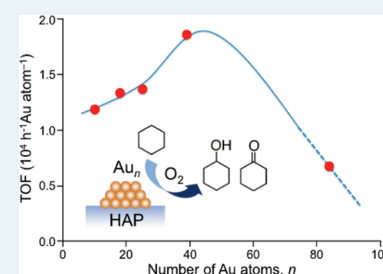
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**S** Supporting Information

**ABSTRACT:** In this work, we synthesized gold clusters, Au<sub>n</sub> (*n* = 10, 18, 25, 39), with atomically controlled sizes on hydroxyapatite (HAP) and studied the catalysis for aerobic oxidation of cyclohexane. These Au<sub>n</sub>/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 18 500 h<sup>-1</sup> Au atom<sup>-1</sup> at *n* = 39, and thereafter decreased with a further increase in *n* up to *n* ~ 85. This finding provides a fundamental insight into size-specific catalysis of gold in the cluster regime (diameter < 2 nm) and a guiding principle for rational design of Au cluster-based catalysts.

**KEYWORDS:** Au clusters, size effect, aerobic oxidation, hydroxyapatite



Gold nanoparticles (AuNPs) on solid supports have been studied extensively as promising catalysts for a variety of oxidation reactions. In particular, increased interest has been focused on using O<sub>2</sub> as an oxidant, from the viewpoint of green chemistry.<sup>1–6</sup> Extensive studies have revealed that the size (diameter) of AuNPs has a significant influence on their catalytic properties: the catalytic activity increases with decreasing size.<sup>7,8</sup> However, fundamental questions remain unanswered: How does the catalytic activity evolve in the cluster regime (diameter < 2 nm), and how does the catalytic activity correlate with that of single Au atoms?<sup>9,10</sup> To answer these questions, it is essential to synthesize a series of Au<sub>n</sub> clusters with atomically controlled sizes of *n* (number of Au atoms) on solid supports. Soft landing of size-selected, bare Au<sub>n</sub> clusters onto supports is a straightforward method, but requires sophisticated equipment; a mixture of Au<sub>6–10</sub> has been successfully immobilized on TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> using this method.<sup>11</sup> Diameter-controlled AuNPs have been synthesized by removing the ligands from monodisperse AuNPs that are protected by ligands (thiolates/phosphines) on supports.<sup>12–15</sup> This approach has been successfully applied to the synthesis of size-controlled Au<sub>n</sub> clusters (Au<sub>55</sub> on silica,<sup>16</sup> Au<sub>11</sub> on mesoporous silica (SBA-15),<sup>17</sup> and Au<sub>25</sub> on hydroxyapatite (HAP).<sup>18</sup>); however, to the best of our knowledge, systematic studies on the size effect on the catalysis in the sub-2 nm region have not been conducted so far.

The aim of the present work is to develop the size-controlled synthesis of Au<sub>n</sub> clusters on solid supports and to reveal the effect of cluster size on catalysis in aerobic oxidation in the sub-2 nm region. To this end, we utilized a series of glutathionate (GS)-protected Au<sub>n</sub> clusters with well-defined size *n* as Au precursors.<sup>19</sup> HAP (Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>) was used as the support<sup>20–22</sup> with the expectation that Au<sub>n</sub>(SG)<sub>*m*</sub> passivated by tripeptide molecules (glutathionates) are adsorbed as efficiently as other

biomolecules via hydrogen bonding and/or electrostatic interaction.<sup>23</sup> The catalytic activities of the size-selected Au<sub>n</sub> clusters on HAP were compared for examining their use in the aerobic oxidation of cyclohexane, which is industrially important because the products, cyclohexanone and cyclohexanol (Ketone/Alcohol or KA-oil), are key intermediates for the production of nylon-6 and nylon-66, but remains a challenge in modern chemistry.<sup>24</sup> We hope that this work will deepen understanding of the intrinsic size effect of gold catalysis and provide a guiding principle to design Au cluster-based catalysts.

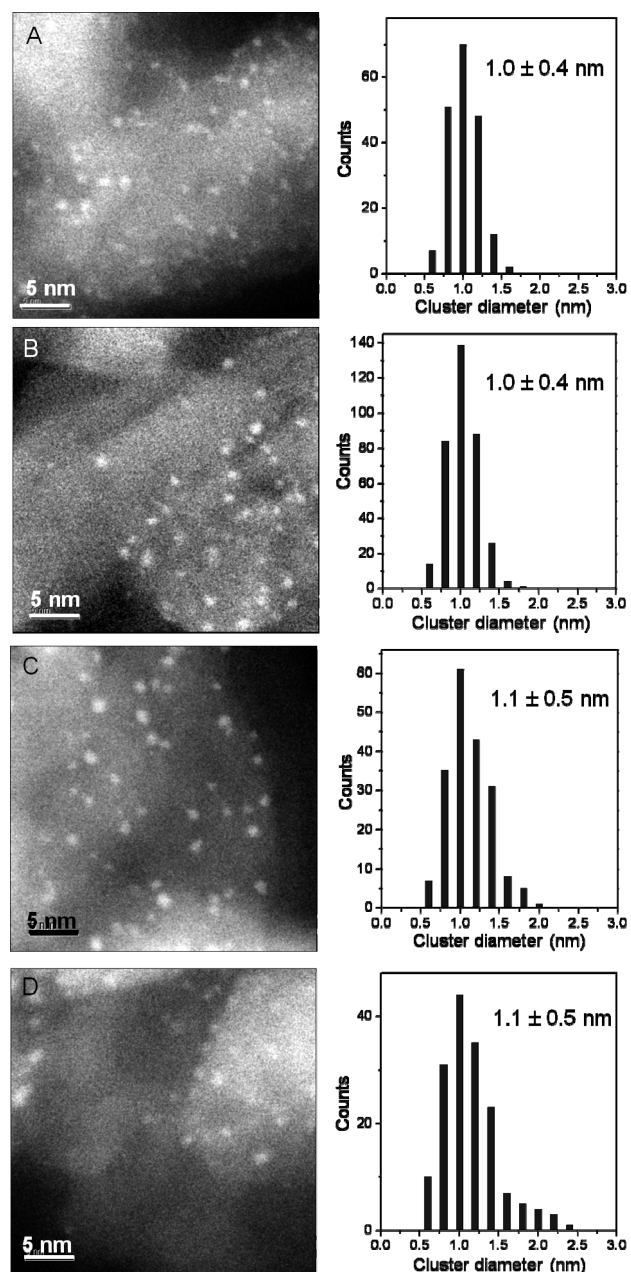
Size-controlled Au<sub>n</sub> clusters on HAP were synthesized in two steps. The first step was adsorption of Au<sub>n</sub>(SG)<sub>*m*</sub> with well-defined compositions on HAP to produce the composite Au<sub>n</sub>(SG)<sub>*m*</sub>/HAP. As Au precursors, we selected Au<sub>n</sub>(SG)<sub>*m*</sub> with (*n*, *m*) = (10, 10), (18, 14), (25, 18), and (39, 24); the Au<sub>18</sub>(SG)<sub>14</sub> and Au<sub>25</sub>(SG)<sub>18</sub> samples were chemically pure, whereas the Au<sub>10</sub>(SG)<sub>10</sub> and Au<sub>39</sub>(SG)<sub>24</sub> samples were contaminated with a small amount of Au<sub>11</sub>(SG)<sub>11</sub>/Au<sub>12</sub>(SG)<sub>12</sub> and Au<sub>38</sub>(SG)<sub>24</sub>, respectively.<sup>19</sup> The second step was calcination of the Au<sub>n</sub>(SG)<sub>*m*</sub>/HAP composites to remove the GS ligands.<sup>18,25</sup> The resulting catalysts are hereafter referred to as Au<sub>n</sub>/HAP.

The Au<sub>n</sub>(SG)<sub>*m*</sub>/HAP composites were obtained by filtration of the mixture of HAP and Au<sub>n</sub>(SG)<sub>*m*</sub> in basic water (pH ~ 9.8). The filtrates were colorless, indicating complete adsorption of Au<sub>n</sub>(SG)<sub>*m*</sub> on HAP (Figure S1 of the Supporting Information). The amount of Au adsorbed is estimated from the molar extinction coefficient<sup>19</sup> to be 0.2 wt % with respect to that of HAP. The reflectance spectra of Au<sub>n</sub>(SG)<sub>*m*</sub>/HAP exhibited profiles similar

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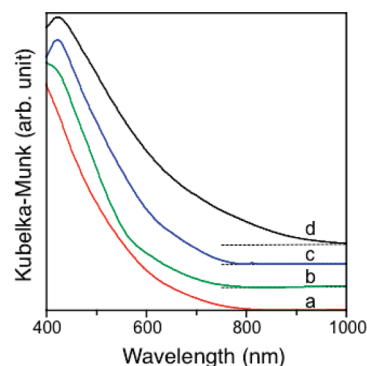
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**Figure 1.** Representative HAADF-STEM images of  $Au_n/HAP$  and cluster size distributions; the  $n$  values are (A) 10, (B) 18, (C) 25, and (D) 39.

to the absorption spectra of  $Au_n(SG)_m$  (Figure S2 of the Supporting Information).<sup>19</sup> This result indicated that  $Au_n(SG)_m$  were adsorbed on HAP with their form intact. The following improvements were made to the preparation method of  $Au_n(SG)_m/HAP$ <sup>18</sup> to minimize the possibility of aggregation of Au clusters during the calcination: (1) The surface area of HAP was increased from 20–30 to  $\sim 100$   $m^2 g^{-1}$  (Table S1 of the Supporting Information) using the synthesis method given in ref 26. (2) The Au loading was reduced from 0.5 to 0.2 wt %. (3) The pH of the dispersion was set  $\sim 9.8$  higher than the  $pK_a$  values (2.12, 3.53, 8.66, 9.12) of GSH (Figure S3 of the Supporting Information). These improvements reduced the density of adsorbed  $Au_n(SG)_m$  and allowed them to be adsorbed more homogeneously over the HAP support through the electrostatic repulsion between the carboxylate moieties<sup>27</sup> of the GS ligands.

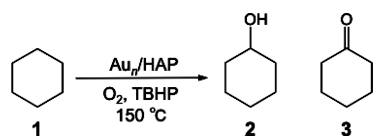


**Figure 2.** Diffuse reflectance UV-vis spectra of  $Au_n/HAP$ ; the  $n$  values are (a) 10, (b) 18, (c) 25, and (d) 39.

The  $Au_n/HAP$  catalysts were prepared by calcinating the  $Au_n(SG)_m/HAP$  composites at 300 °C for 2 h in vacuo.<sup>18</sup> The effective removal of the GS ligands was confirmed by inductively coupled plasma (ICP) analysis and X-ray photoelectron spectroscopy (XPS). The sulfur content in  $Au_{25}(SG)_{18}/HAP$  (58 ppm), for example, was reduced to 5 ppm in  $Au_{25}/HAP$ , which was comparable to the amount of sulfur impurity in HAP. Preliminary XPS measurement on  $Au_{25}(SG)_{18}/HAP$  and  $Au_{25}/HAP$  (data not shown) also showed that the sulfur content after the calcination is negligibly small. Au loading was confirmed to be 0.17–0.21 wt % by the analysis (Table S1). Calcination under the conditions mentioned above did not alter the structure of the HAP (Figure S4 of the Supporting Information).

Transmission electron microscopy (TEM) on  $Au_n/HAP$  revealed no appreciable aggregation of the Au clusters during the calcination. Figure 1 shows typical high angle annular dark field-scanning TEM (HAADF-STEM) images and size distributions for Au clusters obtained by counting more than 160 particles. The average diameters ( $d_{av}$ ) of the Au clusters in  $Au_n/HAP$  for  $n = 10, 18, 25, 39$  appeared to be 1.0–1.1 nm, regardless of the size of the  $Au_n(SG)_m$  precursors. Similar results were also obtained by the conventional TEM observation (Figure S5 of the Supporting Information). Although neither HAADF-STEM nor TEM could differentiate the cluster size among the four  $Au_n/HAP$  samples, as anticipated from the spatial resolutions of these methods, we can conclude that the aggregation of Au clusters during the calcination is negligible. A direct method to probe the number of Au atoms in each cluster is to analyze the contrast of the individual clusters in the HAADF-STEM images,<sup>28,29</sup> which is a subject of our future study. Instead, we compared the optical spectra of  $Au_n/HAP$  composites (Figure 2). The spectra show different profiles, and the optical onset for  $n = 39$  is located at notably longer wavelength than the others. These observations indicated that the Au clusters of  $Au_n/HAP$  were composed of different numbers of atoms.

Although the results in Figures 1 and 2 suggest that the size of the Au clusters is preserved during the calcination, the distributions of the diameters are broader and the optical spectra are smoother than those expected for single-sized Au clusters. We believe that these observations are partly accounted for in the formation of structural isomers of the Au clusters. An ensemble of structural isomers produced in the calcination of  $Au_n(SG)_m$  will give rise to polydisperse TEM images and smooth optical spectra because the spectral profiles may vary among the isomers. Strong interaction between the Au and  $PO_4^{3-}$  moieties<sup>30</sup> of HAP additionally contributes to the modification of the structures of the Au clusters.

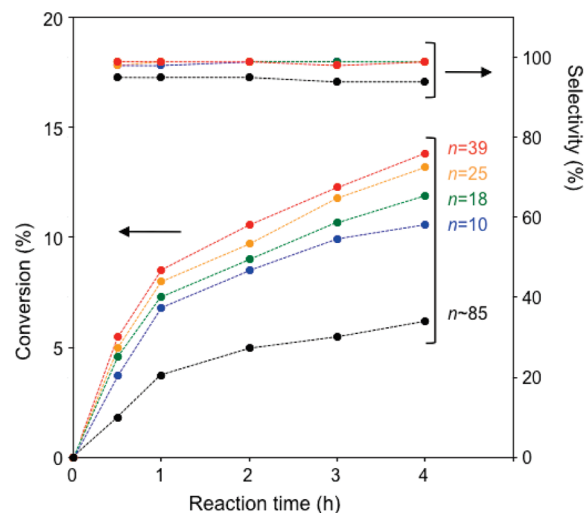
Table 1. Oxidation of Cyclohexane<sup>a</sup>

entry	catalyst	conv (%) <sup>c</sup>	selectivity (%) <sup>b</sup>		TOF ( $\times 10^4 \text{ h}^{-1}$ ) <sup>d</sup>
			2	3	
1	Au <sub>10</sub> /HAP	11.6	58	41	1.19
2	Au <sub>18</sub> /HAP	12.9	49	50	1.33
3	Au <sub>25</sub> /HAP	14.2	50	49	1.37
4	Au <sub>39</sub> /HAP	14.9	50	49	1.85
5	Au <sub>~85</sub> /HAP	6.7	53	41	0.68
6	Au <sub>25</sub> /HAP <sub>second</sub>	13.9	51	47	
7	Au <sub>25</sub> /HAP <sub>third</sub>	13.7	50	48	

<sup>a</sup> The reactions were carried out with Au<sub>n</sub>/HAP (100 mg) and TBHP (10 mg) in **1** (10 mL) under an O<sub>2</sub> atmosphere (1 MPa, ~30 mL) at 150 °C for 4 h. <sup>b</sup> Selectivity was determined as the ratio of the yield of each product to the total yield of products. <sup>c</sup> Conversion was calculated on the basis of the amount of **1** recovered. <sup>d</sup> TOF was calculated from the amount of **1** recovered for the following reaction conditions and materials: Au<sub>n</sub>/HAP (100 mg), TBHP (10 mg), **1** (15 mL), and O<sub>2</sub> (1 MPa, ~100 mL) at 150 °C for 30 min.

Aerobic oxidation of cyclohexane (**1**) catalyzed by AuNPs ( $d_{\text{av}} > 3 \text{ nm}$ ) supported on various supports has been studied by several groups.<sup>31–37</sup> We investigated how the catalytic activity of Au<sub>n</sub>/HAP ( $n = 10, 18, 25, 39$ ) evolves in the size range  $d_{\text{av}} < 2 \text{ nm}$  using this reaction as a test reaction. As a reference, we also studied the catalysis of larger Au clusters ( $d_{\text{av}} = 1.4 \pm 0.6 \text{ nm}$ , 0.2 wt % of Au) on HAP prepared by a conventional adsorption method (Figures S6 and S7 of the Supporting Information). This catalyst is referred to as Au<sub>~85</sub>/HAP because the average diameter of the Au clusters corresponds to that of Au<sub>85</sub> on the assumption that the clusters have the same density as bulk Au.

Table 1 summarizes the catalytic performance of Au<sub>n</sub>/HAP for the oxidation of **1** under an O<sub>2</sub> atmosphere (1 MPa) at 150 °C. No conversion was observed in the absence of gold, which confirms that the Au clusters play an essential role in the catalytic conversion. The addition of a small amount of TBHP ( $[\text{TBHP}]/[\text{1}] = 1.2 \times 10^{-3}$ ) was essential to initiate the reaction,<sup>34</sup> suggesting that this oxidation proceeds via a complex radical chain mechanism.<sup>24,37</sup> In all the cases, cyclohexanol (**2**) and cyclohexanone (**3**) were obtained as the primary products with nearly equivalent yields; adipic acid was not formed. The conversion of **1** after 4 h gradually increased from 11.6% to 14.9% for the increase in  $n$  from 10 to 39 (entries 1–4) and decreased to 6.7% for  $n \sim 85$  (entry 5). To check the lot-to-lot reproducibility of the results, we tested the catalytic activity for three Au<sub>25</sub>/HAP catalysts synthesized independently. The conversions observed for each of the catalysts were similar with a typical standard deviation of less than 1% (Table S2 of the Supporting Information). This result clearly shows how a difference in cluster size of several atoms affects the catalytic activity. The Au<sub>n</sub>/HAP catalysts could be reused at least three times without any noticeable loss in activity (entries 3, 6, 7). The recyclability is ascribed to the durability of the Au<sub>n</sub>/HAP catalysts under the conditions as evidenced

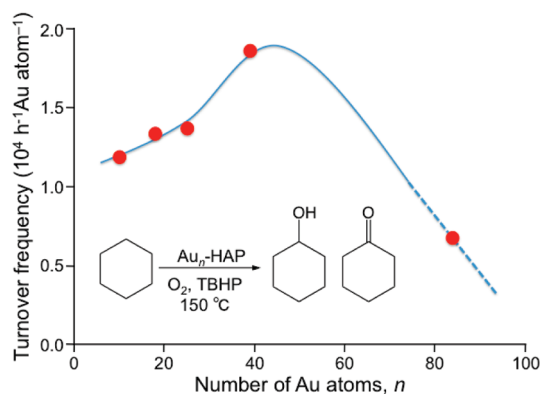


**Figure 3.** Time dependence of the conversion of **1** and the total selectivity of **2** and **3** by Au<sub>n</sub>/HAP. The reactions were carried out with Au<sub>n</sub>/HAP (100 mg) and TBHP (10 mg) in **1** (15 mL) under an O<sub>2</sub> atmosphere (1 MPa) at 150 °C. During the reaction, the O<sub>2</sub> gas was continuously supplied from the gas cylinder to keep the pressure constant.

by the optical spectra (Figure S8 of the Supporting Information) and TEM images (Figure S9 of the Supporting Information) of Au<sub>25</sub>/HAP before and after the catalytic usage.

We studied the catalytic behavior of Au<sub>n</sub>/HAP in more detail under a constant pressure (1 MPa) of O<sub>2</sub>, since most of the O<sub>2</sub> in the autoclave was consumed after 4 h under the conditions employed above (Table 1). Figure 3 shows time dependence of the conversion of **1** and total selectivity for **2** and **3** (KA-oil) by Au<sub>n</sub>/HAP. Conversions increased with a reaction time for all the catalysts. The total selectivities for **2** and **3** were nearly constant, regardless of the conversion, in sharp contrast to the results reported in refs 34 and 36. The selectivities for KA-oil were as high as ~99% for smaller Au<sub>n</sub>/HAP ( $n = 10–39$ ), whereas it was reduced slightly to ~95% for Au<sub>~85</sub>/HAP. The selectivities for Au<sub>n</sub>/HAP ( $n = 10–39$ ) are among the highest in the literature: 92–97% for Au (>2 nm)/MCM-41,<sup>32</sup> 94–96% for Au (2.8, 6.5, 8.8 nm)/SBA-15,<sup>33</sup> 10–23% for Au/graphite,<sup>34</sup> 84–87% for Au (3–6 nm)/Al<sub>2</sub>O<sub>3</sub>,<sup>35</sup> 92% for Au (3–8 nm)/TiO<sub>2</sub>/SiO<sub>2</sub>,<sup>36</sup> 65% for Au (~5 nm)/TiO<sub>2</sub>,<sup>37</sup> 60% for Au (~5 nm)/Al<sub>2</sub>O<sub>3</sub>,<sup>37</sup> and 71% for Au (~4 nm)/SBA-15.<sup>37</sup>

The time evolution of the conversion shown in Figure 3 indicates that the activities increased in the order of Au<sub>~85</sub> < Au<sub>10</sub> < Au<sub>18</sub> < Au<sub>25</sub> < Au<sub>39</sub>. The catalytic activities of Au<sub>n</sub>/HAP were compared more quantitatively by using the TOF values, which is defined as the number of molecules of **1** converted per Au atom per hour.<sup>31–36</sup> The TOF values were tentatively calculated from conversions at the initial stage of the reaction (0.5 h). The TOF values of Au<sub>n</sub>/HAP thus obtained are listed in Table 1. They are comparable to or higher than those of Au catalysts reported previously (11214 h<sup>-1</sup> for Au (>2 nm)/MCM-41<sup>32</sup> and 16136 h<sup>-1</sup> for Au (3–6 nm)/Al<sub>2</sub>O<sub>3</sub><sup>35</sup>) but smaller than the highest value in the literature, which amounts to 40 133 h<sup>-1</sup> for Au (3–8 nm)/TiO<sub>2</sub>/SiO<sub>2</sub>.<sup>36</sup> Figure 4 shows a plot of the TOF values as a function of the cluster size,  $n$ . The TOF values monotonically increase with an increase in the size in the  $n$  range from 10 to 39 but decrease in the  $n$  range from 39 to ~85. Figure 4 reveals that there is an optimal size of Au clusters in the  $n$  range of 40–80 for



**Figure 4.** TOF values as a function of the cluster size  $n$ . The curve is a guide for the eye.

the aerobic oxidation of cyclohexane. Although it is not clear at this moment how the Au clusters are involved in the complex oxidation processes, the volcano-shaped size dependence in Figure 4 cannot be explained solely in terms of geometrical factors, such as the surface area and density of low-coordination sites on Au clusters. The highest catalytic activity observed in the case of  $\text{Au}_{39}$  may be associated with their unique electronic structures, as suggested by the clear difference in the spectral onsets (Figure 2).

In summary, we have successfully synthesized a series of  $\text{Au}_n$  clusters with well-defined sizes on HAP. The catalytic properties of these ultrasmall  $\text{Au}_n$  clusters were investigated by examining their use in the selective oxidation of cyclohexane to cyclohexanol and cyclohexanone under solvent-free conditions with  $\text{O}_2$  as the oxidant. The total selectivity for cyclohexanol and cyclohexanone reached  $\sim 99\%$ , affording a cyclohexane conversion exceeding 10%. The optimal size of  $\text{Au}_n$  clusters for the aerobic oxidation was determined to correspond to the  $n$  range 39–85.

## EXPERIMENTAL METHODS

**Preparation of Catalysts.** GS-protected Au clusters  $\text{Au}_n(\text{SG})_m$  with  $(n, m) = (10, 10), (18, 14), (25, 18), (39, 24)$  were prepared according to a protocol previously reported by us.<sup>19</sup> HAP was prepared using the synthesis method given in ref 26. The  $\text{Au}_n(\text{SG})_m$  clusters (containing 2 mg Au) were dissolved in water (100 mL), which was adjusted to pH  $\sim 9.8$  using diluted ammonia solution. The mixture was then stirred with HAP (1 g) for 4 h at room temperature. The  $\text{Au}_n(\text{SG})_m/\text{HAP}$  composite was collected by filtration and then calcined in vacuo at 300 °C for 2 h to produce  $\text{Au}_n/\text{HAP}$ . Larger Au clusters ( $d_{\text{av}} = 1.4 \pm 0.6$  nm, 0.2 wt % of Au) on HAP were prepared by a conventional adsorption method (Figures S6 and S7). If the Au clusters are assumed to have the same density as bulk Au, the average diameter corresponds to that of  $\text{Au}_{\sim 85}$ . Thus, this catalyst is referred to as  $\text{Au}_{\sim 85}/\text{HAP}$ , although the Au cluster size is not atomically controlled. The  $\text{Au}_n/\text{HAP}$  catalysts were characterized by reflectance optical spectroscopy, powder XRD, HAADF-STEM, TEM,  $\text{N}_2$  adsorption/desorption isotherm, and ICP.

**Catalytic Test.** The catalytic performance of  $\text{Au}_n/\text{HAP}$  ( $n = 10, 18, 25, 39, \sim 85$ ) for the aerobic oxidation of **1** was studied under solvent-free conditions. Typically, 100 mg of the  $\text{Au}_n/\text{HAP}$  catalysts (containing  $\sim 0.2$  mg of Au, Table S1) and 10 mg of *tert*-butyl hydroperoxide were added to **1** (10 mL) in a Teflon tube placed in a stainless steel autoclave with an internal volume

of 30 mL. After  $\text{O}_2$  (1 MPa) was charged, the reaction mixture in the autoclave was incubated at 150 °C under stirring. After 4 h, the reaction mixture was filtered, and the filtrate was diluted with AcOEt. The chemical identity and the yield of the products were determined by gas chromatography.

## ASSOCIATED CONTENT

**S Supporting Information.** The preparation and characterization of  $\text{Au}_n(\text{SG})_m$ , HAP, and  $\text{Au}_n/\text{HAP}$ . This information is available free of charge via the Internet at <http://pubs.acs.org>.

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