Cite this article as: Chin. J. Catal., 2011, 32: 1149-1155.

ScienceDirect

**RESEARCH PAPER** 

# Comparison of the Catalytic Properties of 25-Atom Gold Nanospheres and Nanorods

# Yan ZHU, Huifeng QIAN, Anindita DAS, Rongchao JIN\*

Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA 15213, USA

**Abstract:** The catalytic properties of two nanocluster catalysts with atomically precisely known structures, icosahedral two-shelled  $Au_{25}(SC_2H_4Ph)_{18}$  nanospheres and biicosahedral  $Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2$  nanorods, were compared. Their catalytic performance in the two reactions of the selective oxidation of styrene and chemoselective hydrogenation of  $\alpha$ , $\beta$ -unsaturated benzalacetone was investigated. The catalytic activities of icosahedral  $Au_{25}(SC_2H_4Ph)_{18}$  nanospheres were superior to those of the bi-icosahedral  $Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_{5}Cl_2$  nanorods for both reactions. The better catalytic performance of the  $Au_{25}(SC_2H_4Ph)_{18}$  nanospheres can be attributed to their unique core-shell ( $Au_{13}/Au_{12}$ ) geometric structure that has an open exterior atomic shell and to their electronic structure with an electron-rich  $Au_{13}$  core and an electron-deficient  $Au_{12}$  shell.

Key words: nanocluster catalyst; icosahedral Au<sub>25</sub>; biicosahedral Au<sub>25</sub>; selective oxidation; selective hydrogenation

The importance of atomic level information on the nature of nanoparticle catalysts has long been recognized in heterogeneous catalysis, but getting this information poses major challenges due to the unavailability of atomically defined nanocatalysts. To gain deeper insight into the fundamental origin of nano-metal catalysis and to explore new catalytic applications, the preparation of well-defined metal catalysts is of critical importance. Recently, major advances have been made in the solution phase synthesis of atomically precise gold nanoclusters by protecting these with thiolate ligands (referred to as  $Au_n(SR)_m$ , where *n* is the number of gold atoms in the particle and *m* is the number of protecting ligands) [1-10]. Examples include Au<sub>25</sub>(SR)<sub>18</sub>, Au<sub>38</sub>(SR)<sub>24</sub>, Au<sub>144</sub>(SR)<sub>60</sub>, and so forth [11–22]. A remarkable feature of these  $Au_n(SR)_m$  nanoclusters is that they can be dispersed as individual clusters composed of a specific number (n) of gold atoms with n tunable from tens to hundreds [7–22]. Relatively small  $Au_n(SR)_m$  nanoclusters (n <ca. 100) exhibit strong quantum size effects [1]. The non-metallic behavior of  $Au_n(SR)_m$  nanoclusters in the range (n) from  $\sim$ ten to a few hundreds is of particular interest to catalysis [23-28]. More importantly, the atom packing structures and unique electronic properties of these  $Au_n(SR)_m$ nanoclusters [19,29,30] can permit the correlation of particle

structure with catalytic properties, which would allow the identification of the catalytically active sites on gold nanoclusters [31].

In our previous work, we have made important advances in gold nanocatalysis using well defined Au<sub>n</sub>(SR)<sub>m</sub> nanoclusters as catalysts for selective oxidation and hydrogenation processes, such as the selective oxidation of styrene and the chemoselective hydrogenation of  $\alpha$ ,  $\beta$ -unsaturated ketones (or aldehydes) [23,31-33]. Concerning the 25 gold atom nanoclusters, two different structures have been reported - an icosahedral two-shelled  $[Au_{25}(SC_2H_4Ph)_{18}]^q$  (q = -1, 0) nanosphere [29,30] and a biicosahedral  $[Au_{25}(PPh_3)_{10}(SC_2H_5)_5Cl_2]^{2+}$ rod [34]. Recently, we have developed a size-focusing method that employed phosphine-capped, polydispersed Au nanoparticles as a common starting material to synthesize  $[Au_{25}(SG)_{18}]^{-}$  nanospheres (1.27 nm diameter, where SG = glutathione) and [Au<sub>25</sub>(PPh<sub>3</sub>)<sub>10</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>5</sub>Cl<sub>2</sub>]<sup>2+</sup> nanorods (0.8  $nm \times 1.38$  nm), respectively, by two-phase and one-phase thiol etching [35]. The aim was to use these two Au<sub>25</sub> structures (sphere vs. rod) in a comparative study of their catalytic properties in the hope of finding the factors that affect their catalytic performance.

Here, we chose the selective oxidation of styrene and selec-

\*Corresponding author. Tel: +1-412-268-9448; Fax: +1-412-268-1061; E-mail: rongchao@andrew.cmu.edu

This work was supported by CMU, AFOSR, and NIOSH.

Received 8 February 2011. Accepted 6 April 2011.

Copyright © 2011, Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Published by Elsevier BV. All rights reserved. DOI: 10.1016/S1872-2067(10)60238-0

tive hydrogenation of  $\alpha$ , $\beta$ -unsaturated benzalacetone as the reactions for comparing the catalytic properties of icosahedral two-shelled Au<sub>25</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>18</sub> spheres and biicosahedral [Au<sub>25</sub>(PPh<sub>3</sub>)<sub>10</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>5</sub>Cl<sub>2</sub>]<sup>2+</sup> rods. The results clearly demonstrated that the icosahedral Au<sub>25</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>18</sub> nanospheres had a significantly higher catalytic activity than the biicosahedral Au<sub>25</sub> nanorods. Based on this, we discuss the factors that are potentially important for catalytic properties, including cluster shape (sphere vs. rod), arrangement of surface atoms, and electronic structures. This work provides the first example of looking at how the atomic structure of nanoparticle catalysts affects their catalytic properties.

# **1** Experimental

#### 1.1 Preparation of Au<sub>25</sub> nanocluster

The detailed synthesis and characterization of Au<sub>25</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>18</sub> spherical nanoclusters were reported in our previous work [29]. Briefly, HAuCl<sub>4</sub>·3H<sub>2</sub>O (0.4 mmol) was dissolved in water (5 ml). Tetraoctylammonium bromide (TOAB, 0.47 mmol) was dissolved in toluene (10 ml). The two solutions were combined in a 25 ml three-neck round bottom flask. The solution was vigorously stirred with a magnetic bar to facilitate the phase transfer of the gold(III) salt into the toluene phase. After ~15 min, the phase transfer was completed, leaving a clear aqueous phase at the bottom of the flask. The aqueous phase was removed using a glass pipette. The toluene solution of gold(III) was purged with N<sub>2</sub> and cooled to 0 °C in an ice bath over a period of ~30 min under magnetic stirring. Phenylethylthiol (PhC<sub>2</sub>H<sub>4</sub>SH, 0.17 ml) was added. The deep red solution turned to faint yellow over a period of 5 min, and finally to clear over 1 h. After the solution turned clear, a freshly made aqueous solution of NaBH<sub>4</sub> (4 mmol in  $\sim$ 7 ml ice cold water) was quickly added. The reaction was allowed to proceed overnight. Then, ethanol (20 ml) was added to separate Au<sub>25</sub> nanoclusters from TOAB and the reaction byproducts. The Au<sub>25</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>18</sub> clusters (denoted as i-Au<sub>25</sub>) were collected after removing the supernatant.

The details of the two-step synthesis of  $[Au_{25}(PPh_3)_{10}-(SC_2H_4Ph)_5Cl_2]^{2+}$  rod nanoclusters were reported in [35]. Briefly, the first step was to prepare triphenylphosphine (PPh\_3)-protected Au nanoparticles as follows. HAuCl\_4·3H\_2O (0.118 g, 0.3 mmol, dissolved in 5 ml H\_2O) and TOAB (0.190 g, 0.348 mmol, dissolved in 10 ml toluene) were combined in a three-neck round bottom flask. After the solution was vigor-ously stirred for about 15 min to effect the phase transfer of Au(III) into the toluene phase, the aqueous phase became clear and the toluene phase turned dark red, indicating that Au(III) was completely transferred to the toluene phase. The aqueous phase was removed and 0.235 g (0.9 mmol) of PPh\_3 was added to the toluene solution under vigorous stirring. The toluene solution became whitish cloudy. Then, NaBH\_4 (0.034 g, 0.9

mmol, dissolved in 5 ml ethanol) was injected rapidly. The solution immediately turned dark. The reaction was allowed to proceed for 2 h at room temperature in air. A black product (containing PPh<sub>3</sub>-protected Au nanoparticles) was obtained after the rotary evaporation of the solvent (toluene). The black product was washed several times with water and hexane to remove excess PPh<sub>3</sub> and TOAB. Then, the black product was dissolved in chloroform. Unreacted gold salt (i.e. Au(PPh<sub>3</sub>)Cl) was removed by precipitating the black product by adding pentane to the chloroform solution. The black product (~100 mg) obtained was collected. Thermogravimetric (TG) analysis showed that the organic content in the nanoparticles was about 50 wt%. For the second step, size-focusing conversion of polydisperse Au nanoparticles (1-3 nm) into biicosahedral Au<sub>25</sub> nanoclusters (formula:  $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]^{2+}$ , counterion: Cl) was achieved by adding PhC<sub>2</sub>H<sub>4</sub>SH to phosphine-protected Au nanoparticles (~20 mg, dissolved in 20 ml CH<sub>2</sub>Cl<sub>2</sub>). The molar ratio of PhC<sub>2</sub>H<sub>4</sub>SH to Au atoms was controlled at  $PhC_2H_4SH/Au = 6:1$ ; where it should be noted that PhC<sub>2</sub>H<sub>4</sub>SH was in large excess. The solution was vigorously stirred for 12 h at room temperature. The product (denoted as bi-Au<sub>25</sub>) was obtained after drying the solution by rotary evaporation, followed by further purification by washing with hexane and extraction with ethanol.

# 1.2 Preparation of catalyst

The CeO<sub>2</sub> nanopowder was purchased from Aldrich and used as received. CeO<sub>2</sub> supported Au<sub>25</sub> nanoclusters were obtained by mixing a specific amount of CeO<sub>2</sub> with a CH<sub>2</sub>Cl<sub>2</sub> solution of the Au<sub>25</sub> nanoclusters, followed by stirring for 24 h. The solution was then dried under a N<sub>2</sub> gas stream. To calcine the Au<sub>25</sub>/CeO<sub>2</sub> catalysts, a thermal treatment in a vacuum oven was performed.

# 1.3 Catalytic tests

The catalytic selective oxidation of styrene reaction was carried out at atmospheric pressure. CeO<sub>2</sub> supported Au<sub>25</sub> catalysts (100 mg powder, 1 wt% loading of gold clusters), styrene (10 mmol), and *t*-butyl hydroperoxide (TBHP, 38 mmol) were mixed in CH<sub>3</sub>CN (solvent, 15 ml) in a 50 ml sealed glass reactor. Then the mixture was heated to 82 °C under constant vigorous stirring in an oil bath for ~20 h. The solvent was removed by rotary evaporation and the products were analyzed by nuclear magnetic resonance (<sup>1</sup>H NMR) spectroscopy. <sup>1</sup>H NMR spectra were collected on a Bruker Avance<sup>TM</sup> 300 MHz spectrometer. The conversion and selectivity were calculated by integrating the NMR peak areas.

For the selective hydrogenation of benzalacetone, benzalacetone (0.1 mmol) was dissolved in a mixed solvent (5 ml toluene and 5 ml ethanol) in a 50-ml three-neck glass flask. CeO<sub>2</sub> supported Au<sub>25</sub> catalysts (100 mg powder, 1 wt% loading of gold clusters) were added. The reaction was initiated by introducing a H<sub>2</sub> flow (under atmospheric pressure). The reaction temperature was 0 °C. The reaction was typically allowed to proceed under continuous H<sub>2</sub> flow for ~4 h. The products were analyzed by <sup>1</sup>H NMR spectroscopy.

# 2 Results and discussion

# 2.1 Atomic structure of the $Au_{25}$ nanospheres and nanorods

The crystal structures of i-Au<sub>25</sub> and bi-Au<sub>25</sub> have been reported previously [29,30,34]. These are shown in Fig. 1, where for clarity, the thiolate and phosphine ligands are represented only by S and P atoms, respectively.

The spherical Au<sub>25</sub> cluster (1.27 nm diameter, Au surface-to-surface distance) adopts a core-shell structure and can be viewed as an icosahedral Au<sub>13</sub> core (Fig. 1(a), magenta) encapsulated by an exterior shell consisting of the 12 remaining gold atoms (Fig. 1(a), green) [29,30]. The entire particle is protected by eighteen thiolate ligands. Both experiment and theory indicated that the Au<sub>13</sub> icosahedral core is relatively electron-rich due to the presence of 8e (for anionic i-Au<sub>25</sub><sup>-</sup>) or 7e (for neutral i-Au<sub>25</sub><sup>0</sup>), while the exterior Au<sub>12</sub> shell is relatively electron-deficient due to the covalent bonding of Au-S [36]. It should be noted that each thiolate ligand formally localizes one valence electron of Au 6*s*, that is, 25(Au)-18(ligands)+1 = 8e for Au<sub>25</sub>(SR)<sub>18</sub><sup>-</sup>.

The Au<sub>25</sub> rod (0.8 nm diameter  $\times$  1.38 nm length, Au surface-to-surface distance) structure may be viewed as two icosahedrons fused together by sharing a common vertex (i.e. 13+13-1 = 25 atoms, Fig. 1(b)). Its overall shape resembles a rod. The entire structure is protected by 5 thiolates at the waist, 10 phosphines evenly distributed on the two icosahedrons, and two chloride ligands on the rod ends. Concerning the electronic properties of the Au<sub>25</sub> rod, phosphine only forms dative bonds with Au and hence does not localize the valence electrons of Au 6*s* as thiolate does, while five thiolate and two chloride ligands localize 7e in total, thus, the number of valence electrons of a Au<sub>25</sub> rod are 25-7-2 = 16e after taking the 2+ charge state into consideration. Therefore, each icosahedral unit of the rod may be viewed formally as having 8 valence electrons, and is expected to be relatively electron-rich due to these highly delocalized valence electrons. The difference in electron distribution as compared to the Au<sub>25</sub> sphere could have important effects on their catalytic performance.

For the catalytic experiments, both types of clusters were supported on CeO<sub>2</sub> (powder) with a 1 wt% loading of ligand-protected clusters. We investigated both calcined and uncalcined catalysts for the oxidation and hydrogenation reactions. The ultra-small Au<sub>25</sub> spheres and rods were barely observable under conventional bright field TEM due to the low contrast caused by the ultra-small size. In addition, these ultra-small particles were susceptible to damage by the intense high energy electron beam, thus high resolution TEM characterization of the supported Au<sub>25</sub> particles was difficult. Nevertheless, preliminary characterization by X-ray absorption spectroscopy indicated no changes in the structure and size of Au<sub>25</sub> after its deposition onto ceria as well as after the catalytic reaction. However, calcination at above 180 °C caused the sintering of the Au<sub>25</sub> nanoclusters due to ligand loss.

#### 2.2 Selective oxidation of styrene

We first discuss the catalytic results of the selective oxidation of styrene on the Au<sub>25</sub>/CeO<sub>2</sub> catalysts. The catalytic reaction temperature was maintained at 82 °C, which is well below the thiolate desorption temperature of i-Au<sub>25</sub> (onset temperature  $\approx$  190 °C, Fig. 2(a)) and of bi-Au<sub>25</sub> (onset temperature  $\approx$ 150 °C, Fig. 2(b)), as determined by TG analysis. Note that in bi-Au<sub>25</sub> the loss of triphenylphosphine and Cl ligands starts at 175 °C (Fig. 2(b)). We have also investigated the use of different atmospheres (e.g. N<sub>2</sub>, O<sub>2</sub>) for the TGA analysis and found that the desorption of the ligands did not depend on the atmosphere. Thus, in the case of the uncalcined catalysts, all the ligands remained on the Au<sub>25</sub> spheres and rod clusters during the course of the catalytic reaction. A detailed X-ray absorption spectroscopic analysis will be given in a future



Fig. 1. Atom packing structures of i-Au<sub>25</sub> (a) and bi-Au<sub>25</sub> (b). The core atoms of gold are shown in magenta. Surface gold atoms and ligand atoms are as labeled.



Fig. 2. TG analysis of i-Au<sub>25</sub> (a) and bi-Au<sub>25</sub> (b).

work.

The selective oxidation of styrene can be carried with either peroxide (e.g. TBHP) or O<sub>2</sub>. Here we chose TBHP as the oxidant. The catalytic reaction of styrene oxidation was carried out in the liquid phase (acetonitrile as the solvent). As shown in Table 1, the catalytic activity of i-Au<sub>25</sub>/CeO<sub>2</sub> was significantly higher than that of bi-Au<sub>25</sub>/CeO<sub>2</sub> (Table 1, entries 1 and 3). 95% conversion of styrene (TOF:  $1.3 \times 10^{-4}$  mol/(g·s)) was obtained with the uncalcined i-Au<sub>25</sub>/CeO<sub>2</sub> catalyst, but there was only 57% conversion (TOF:  $8 \times 10^{-5}$  mol/(g·s)) with the uncalcined bi-Au<sub>25</sub>/CeO<sub>2</sub> catalyst. Interestingly, both catalysts gave similar selectivities for epoxide (97% vs. 95%), which indicated that the different structures of the 25-gold-atom cluster catalysts had little effect on the selectivity, although a significant effect on the catalytic activity was observed. It is worth noting that the activity (95%) and epoxide selectivity (97%) obtained on the i-Au<sub>25</sub>/CeO<sub>2</sub> catalyst were much higher than those reported for conventional gold catalysts [37-42]. We have previously reported for i-Au25-catalyzed oxidation of styrene in toluene by  $O_2$  [23] or TBHP [32] that the catalytic activity with TBHP as the oxidant was significantly higher than that with O<sub>2</sub>. This is because TBHP is much easier to activate than O<sub>2</sub>. On the other hand, the difference in selectivity (97% epoxide in the present work vs. ~100% for benzaldehyde in the previous work [33]) seems to be due to a promotion effect of acetonitrile. Here, we

Table 1Catalytic performance of two types of  $Au_{25}/CeO_2$  catalysts forthe selective oxidation of styrene by peroxide TBHP

Entry	Catalyst	Conversion	Selectivity (%)			
		(%)	Epoxide	Benzaldehyde	Acetophenone	
1	i-Au <sub>25</sub> /CeO <sub>2</sub> <sup>a</sup>	95	97	3	trace	
2	i-Au <sub>25</sub> /CeO <sub>2</sub> <sup>b</sup>	49	95	4	1	
3	bi-Au <sub>25</sub> /CeO <sub>2</sub> <sup>a</sup>	57	95	3	2	
4	bi-Au <sub>25</sub> /CeO <sub>2</sub> <sup>c</sup>	46	93	5	2	
5	bi-Au <sub>25</sub> /CeO <sub>2</sub> <sup>b</sup>	42	95	5	trace	
6	$CeO_2$	14	81	14	5	

Reaction conditions: Au<sub>25</sub>/CeO<sub>2</sub> 100 mg, styrene 10 mmol, TBHP 38 mmol, solvent CH<sub>3</sub>CN 15 ml, 82 °C, 20 h.

<sup>a</sup>Catalysts without thermal treatment before catalytic tests.

<sup>b</sup>Catalysts with thermal treatment at 260 °C for 2 h.

°Catalysts with thermal treatment (in vacuum oven) at 170 °C for 2 h.

focus on comparing the catalytic performances of the i-Au<sub>25</sub> and bi-Au<sub>25</sub> catalysts.

During the catalytic reaction, the thiolate ligands will remain on both the i-Au<sub>25</sub> and bi-Au<sub>25</sub> catalysts since the reaction temperature (82 °C) was well below the ligand desorption temperature. Reactant molecules such as styrene can readily penetrate the ligand shell of the Au<sub>25</sub> clusters to reach the cluster surface where styrene and TBHP are adsorbed and subsequently react on the surface. To further investigate the two types of Au<sub>25</sub> catalysts, we performed a thermal pretreatment of the catalysts before the catalytic reaction. The thermal treatment step removes surface ligands at least partially (depending on the temperature), so that the Au<sub>25</sub> surface becomes more accessible to reactant molecules. This would give a higher catalytic activity, but the negative effect is that the (partial) loss of protecting ligands can cause cluster sintering if the cluster/support interaction is not strong enough to retain the clusters. If the latter effect dominates, the resulting larger Au nanoparticles would be less catalytically active. According to the TG results (Fig. 2), calcination at 260 °C leads to a complete removal of ligands from both types of Au<sub>25</sub> cluster surfaces. Catalytic tests with these catalysts thermally treated at 260 °C showed a drop in activity (Table 1, entries 2 and 5). A significant drop of activity from 95% to 49% was observed for the calcined i-Au<sub>25</sub>/CeO<sub>2</sub> catalyst, while the calcined bi-Au<sub>25</sub>/CeO<sub>2</sub> catalyst showed a smaller drop from 57% to 42%. The selectivity for styrene epoxide was essentially unchanged and both catalysts still gave 95% selectivity. The drop in activity for both types of Au<sub>25</sub> catalysts indicated that cluster sintering had occurred, which was also indicated by the color change of the catalysts to red. The negative effect of thermal pretreatment was dominant for the calcined catalysts. This is reasonable since large Au nanoparticles (> 3-5 nm) are known to be less catalytically active. The reason the i-Au<sub>25</sub> catalyst was much more sensitive to the thermal pretreatment than bi-Au<sub>25</sub> was because of their stability difference. The majority of i-Au<sub>25</sub> clusters have aggregated into larger nanoparticles after the 260 °C pretreatment, while with bi-Au<sub>25</sub>, sintering occurred to a lesser extent.

For the bi-Au<sub>25</sub> catalyst, the TG results (Fig. 2) showed a two

stage desorption of the surface ligands. Thus, one can selectively remove the thiolate ligands (at  $\sim 175$  °C) while keeping PPh<sub>3</sub> and Cl ligands, as opposed to the 260 °C pretreatment that removed all the ligands (SR, PPh<sub>3</sub>, and Cl). We thus performed a 170 °C thermal pretreatment of the bi-Au<sub>25</sub>/CeO<sub>2</sub> catalyst. The as-treated bi-Au<sub>25</sub>/CeO<sub>2</sub> catalyst gave 46% conversion of styrene with 93% selectivity for epoxide (Table 1, entry 4), which was somewhat lower than the activity of the uncalcined catalyst (Table 1, entry 3) but slightly higher than the 260 °C pretreated bi-Au<sub>25</sub>/CeO<sub>2</sub> catalyst (Table 1, entry 5). The partial removal of surface thiolate ligands at 170 °C should not cause aggregation of Au<sub>25</sub> rod clusters since the PPh<sub>3</sub> ligands can still protect the cluster well. In our previous work, we found that the structure of i-Au<sub>25</sub> clusters remained unaffected after a thermal treatment up to 160 °C [43]. The above catalytic results indicated that the removal of thiolate ligands led to an increased exposure of surface Au atoms but did not have a distinct effect on the activity. This is consistent with our conclusion above that the presence of ligands is not a critical factor for the catalytic activity, since reactant molecules can readily penetrate the ligand shell [31,32].

Taken together, the above results clearly showed the major influences of the structure (sphere vs. rod) of Au<sub>25</sub> clusters on their catalytic activity. It is worth noting that both types of  $Au_{25}/CeO_2$  catalysts only showed a slight decrease (< 5%) in activity after three cycles and no change in selectivity (not shown). The icosahedral Au<sub>25</sub> cluster adopts a quasi- $D_{2h}$ symmetry and is protected by 18 thiolate ligands (Fig. 1(a)) [29,30]. This structure possesses an open exterior Au shell since the Au<sub>13</sub> core has 20 triangular faces but only twelve of these are capped by the 12 exterior Au atoms, leaving eight triangular Au<sub>3</sub> faces uncapped. This can be clearly seen in the space-filled model (Fig. 3(a)). The eight uncapped sites form volcano-type structures and may act as the catalytically active sites [31-33]. This unique core-shell Au<sub>13</sub>/Au<sub>12</sub> structure was primarily responsible for the facile adsorption and activation of both oxidant (e.g. TBHP) and the -CH=CH<sub>2</sub> group of styrene. Previous work [36,44] has shown distinct differences in the charge distribution on the Au<sub>13</sub> core and the Au<sub>12</sub> shell of a i-Au<sub>25</sub> particle. The presence of partial positive charges on the surface Au atoms (i.e. Au<sup> $\delta^+$ </sup>,  $0 < \delta < 1$ ) in Au<sub>25</sub>(SR)<sub>18</sub> would facilitate the activation of the nucleophilic -CH=CH<sub>2</sub> group of styrene since the positive Au atoms are electrophilic, while the electron-rich Au<sub>13</sub> core would facilitate TBHP activation. Overall, the unique geometric and electronic properties of the Au<sub>25</sub>(SR)<sub>18</sub> clusters make them highly active in the selective oxidation of styrene.

Compared to the icosahedral  $Au_{25}$  sphere, the biicosahedral  $Au_{25}$  rod has a much lower activity as shown above (Table 1). The bi- $Au_{25}$  core is constructed by the vertex sharing of two icosahedral  $Au_{13}$  units. The surface PPh<sub>3</sub> ligands in the bi- $Au_{25}$  structure are much bulkier than the phenylethiolate (SC<sub>2</sub>H<sub>4</sub>Ph) on the i- $Au_{25}$  surface but this factor should not cause such a

large difference in their catalytic activity (95% vs. 57%, Table 1). After ruling out the influence of surface ligands, the remaining factors is the 25-atom metal core. A feature of bi-Au<sub>25</sub> is that all the surface atoms are relatively electron-rich as the 16 valence electrons are evenly delocalized on the two icosahedra. As we discussed above in the case of the core-shell i-Au<sub>25</sub> catalyst, we believe that the electron-rich bi-Au<sub>25</sub> particle should be capable of similarly adsorbing TBHP since the bi-Au<sub>25</sub> surface is electron-rich, but is less suited for activating the C=C bond of styrene since the C=C bond activation prefers positively charged Au sites, which are not available in bi-Au<sub>25</sub>. Some surface Au atoms in the bi-Au<sub>25</sub> cluster (i.e. those Au atoms coordinated to Cl and SC<sub>2</sub>H<sub>4</sub>Ph ligands) are positive, but the highly delocalized 16 valence electrons would compensate for these surface Au atoms bonded to Cl and SC<sub>2</sub>H<sub>4</sub>Ph ligands, and render them less positive, hence, they would have difficulty activating C=C bonds. Apart from the difference in the electronic effects between i-Au<sub>25</sub> and bi-Au<sub>25</sub>, we also stress that the hole-like surface site in the i-Au<sub>25</sub> cluster is important for adsorbing and activating reactant molecules. These unique surface structures are not present in bi-Au<sub>25</sub> (Fig. 3(b)). Theoretical calculations [45] are underway to provide a deeper insight into how the surface atomic structure facilitates adsorption and activation of reactant molecules.

### 2.3 Selective hydrogenation of benzalacetone

Here, we further investigate the catalytic performance of i-Au<sub>25</sub> and bi-Au<sub>25</sub> catalysts in the reaction of the selective hydrogenation of  $\alpha$ , $\beta$ -unsaturated benzalacetone with H<sub>2</sub>. The reaction was performed in the liquid phase at 0 °C by bubbling H<sub>2</sub> into the solution. The results further showed the importance of the atomic packing structure and electronic properties of the Au<sub>25</sub> clusters on their catalytic properties. For the i-Au<sub>25</sub> clusters we have previously reported 100% selectivity for unsaturated alcohols in the hydrogenation reaction of  $\alpha$ , $\beta$ -unsaturated ketones (or aldehydes) with H<sub>2</sub> [31].

Table 2 shows a comparison of  $i-Au_{25}/CeO_2$  and  $bi-Au_{25}/CeO_2$  catalysts for the selective hydrogenation of benzalacetone. The best conversion (34%) was obtained with the uncalcined  $i-Au_{25}/CeO_2$  catalyst with 100% selectivity for unsatu-



Fig. 3. Space filling models of i-Au<sub>25</sub> (a) and bi-Au<sub>25</sub> (b). The arrow indicates one of the unique volcano-like surface sites of the two-shelled Au<sub>25</sub> icosahedral sphere.

**Table 2** Catalytic performance of two types of  $Au_{25}/CeO_2$  catalysts forthe selective hydrogenation of benzalacetone with  $H_2$ 

Entry	Catalyst	Conversion (%)	Selectivity (%)			
			Unsaturated	Saturated	Saturated	
			alcohol	alcohol	ketone	
1	i-Au <sub>25</sub> /CeO <sub>2</sub> <sup>a</sup>	34	100	0	0	
2	i-Au <sub>25</sub> /CeO <sub>2</sub> <sup>b</sup>	4	100	0	0	
3	bi-Au <sub>25</sub> /CeO <sub>2</sub> <sup>a</sup>	9	100	0	0	
4	bi-Au <sub>25</sub> /CeO <sub>2</sub> <sup>c</sup>	4	100	0	0	
5	bi-Au <sub>25</sub> /CeO <sub>2</sub> <sup>b</sup>	3	100	0	0	
6	$CeO_2$	0	0	0	0	

Reaction conditions:  $Au_{25}/CeO_2$  100 mg, benzalacetone 0.1 mmol, toluene 5 ml, ethanol 5 ml, 0 °C, 4 h.

<sup>a</sup>Catalysts without thermal treatment before catalytic tests.

<sup>b</sup>Catalysts with thermal treatment at 260 °C for 2 h.

<sup>e</sup>Catalysts with thermal treatment at 170 <sup>e</sup>C for 2 h. The activity was averaged over two independent measurements.

rated alcohol (Table 2, entry 1). In contrast, uncalcined bi-Au<sub>25</sub>/ $CeO_2$  catalyst only showed 9% conversion (Table 2, entry 3). It is worth noting that the recycled i-Au<sub>25</sub>/CeO<sub>2</sub> catalyst only showed a slight decrease in activity with the same 100% selectivity (not shown).

After the 260 °C thermal pretreatment, i-Au<sub>25</sub>/CeO<sub>2</sub> showed a significant drop in activity (from 34% to 4%), indicating aggregation of Au<sub>25</sub> clusters into larger particles that were essentially inactive in hydrogenation reactions, although they still showed some activity in the selective oxidation reaction (Table 1). As for the bi-Au<sub>25</sub>/CeO<sub>2</sub> catalyst, a thermal pretreatment either at 170 or 260 °C resulted in a drop of catalytic activity (Table 2, entries 4 and 5). Overall, the bi-Au<sub>25</sub> catalyst gave a very low activity in the hydrogenation reaction.

With respect to the relation between the Au<sub>25</sub> structure and catalytic activity, the exterior low coordination Au<sup> $\delta^+$ </sup> atoms in the i-Au<sub>25</sub>/CeO catalyst can readily adsorb H<sub>2</sub> [31,32], while the C=O bond of benzalacetone is activated by the electron-rich Au<sub>13</sub> core. The volcano-like surface structure in i-Au<sub>25</sub> was again identified as critical for the hydrogenation. In contrast, the bi-Au<sub>25</sub> structure and surface charge distribution are not favorable for activating H<sub>2</sub> and C=O bonds, hence, the low activity in the hydrogenation.

# 3 Conclusions

The catalytic properties of two types of Au<sub>25</sub> structures, namely, icosahedral Au<sub>25</sub> nanospheres and biicosahedral Au<sub>25</sub> rods were compared. These two types of nanocluster catalysts have the same number of gold atoms but different structures. The results clearly demonstrated that the icosahedral Au<sub>25</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>18</sub> cluster catalyst was superior to the biicosahedral [Au<sub>25</sub>(PPh<sub>3</sub>)<sub>10</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>5</sub>Cl<sub>2</sub>]<sup>2+</sup> cluster catalyst for both the selective oxidation of styrene to epoxide and chemoselective hydrogenation of  $\alpha$ , $\beta$ -unsaturated benzalacetone to unsaturated alcohol. The activity of the icosahedral Au<sub>25</sub> nanospheres was attributed to their unique atomic packing structure (the presence of volcano-like surface sites that act as active sites) and unique electronic properties (electron-rich  $Au_{13}$  core and electron-deficient  $Au_{12}$  shell). This work provided the first demonstration of the influence of the structure of nanogold catalysts on their catalytic activity. For the interaction between Au and the CeO<sub>2</sub> support, X-ray absorption spectroscopic analysis should be able to reveal the nature of the metal-support interaction and its role in enhancing the catalytic activity. Theoretical calculations in future work should reveal more fundamental details of the structure-catalytic property relationship.

# References

- 1 Jin R C. Nanoscale, 2010, 2: 343
- 2 Negishi Y, Nobusada K, Tsukuda T. J Am Chem Soc, 2005, 127: 5261
- 3 Schaaff T G, Whetten R L. J Phys Chem B, 2000, 104: 2630
- 4 Lee D, Donkers R L, Wang G, Harper A S, Murray R W. J Am Chem Soc, 2004, **126**: 6193
- 5 Zhu M Z, Lanni E, Garg N, Bier M E, Jin R. *J Am Chem Soc*, 2008, **130**: 1138
- 6 Jin R C, Qian H F, Wu Z, Zhu Y, Zhu M Z, Mohanty A, Garg N. J Phys Chem Lett, 2010, 1: 2903
- 7 Liu Y, Tsunoyama H, Akita T, Xie S, Tsukuda T. ACS Catal, 2011, 1:2
- 8 Zhu M, Qian H F, Jin R C. J Am Chem Soc, 2009, 131: 7220
- 9 Zhu M, Qian H F, Jin R C. J Phys Chem Lett, 2010, 1: 1003
- 10 Tsunoyama H, Tsukuda T. J Am Chem Soc, 2009, 131: 18216
- 11 Wu Z, Suhan J, Jin R C. J Mater Chem, 2009, 19: 622
- 12 Qian H F, Sfeir M Y, Jin R C. J Phys Chem C, 2010, 114: 19935
- 13 Negishi Y, Kurashige W, Niihori Y, Iwasa T, Nobusada K. Phys Chem Chem Phys, 2010, 12: 6219
- 14 Fields-Zinna C A, Sardar R, Beasley C A, Murray R W. J Am Chem Soc, 2009, 131: 16266
- 15 Angel L A, Majors L T, Dharmaratne A C, Dass A. ACS Nano, 2010, 4: 4691
- 16 Muhammed M A H, Pradeep T. Small, 2011, 7: 204
- 17 Qian H F, Zhu M Z, Andersen U N, Jin R C. *J Phys Chem A*, 2009, **113**: 4281
- 18 Qian H F, Zhu Y, Jin R C. ACS Nano, 2009, 3: 3795
- 19 Qian H F, Eckenhof W T, Zhu Y, Pintauer T, Jin R C. J Am Chem Soc, 2010, 132: 8280
- 20 van Wijngaarden J T, Toikkanen O, Liljeroth P, Quinn B M, Meijerink A. J Phys Chem C, 2010, 114: 16025
- 21 Qian H F, Jin R C. Nano Lett, 2009, 9: 4083
- 22 MacDonald M A, Zhang P, Qian H F, Jin R C. J Phys Chem Lett 2010, 1: 1821
- 23 Zhu Y, Qian H F, Zhu M Z, Jin R C. Adv Mater, 2010, 22: 1915
- 24 Liu Y, Tsunoyama H, Akita T, Tsukuda T. Chem Commun, 2010, **46**: 550
- 25 Corma A, Boronat M, Gonzalez S, Illas F. Chem Commun,

2007, 3371

- 26 Turner M, Golovko V B, Vaughan O P H, Abdulkin P, Berenguer-Murcia A, Tikhov M S, Johnson B F G, Lambert R M. *Nature*, 2008, **454**: 981
- 27 Lopez-Acevedo O, Kacprzak K A, Akola J, Häkkinen H. Nat Chem, 2010, 2: 329
- 28 Pei Y, Shao N, Gao Y, Zeng X C. ACS Nano, 2010, 4: 2009
- 29 Zhu M, Aikens C M, Hollander F J, Schatz G C, Jin R C. *J Am Chem Soc*, 2008, **130**: 5883
- 30 Zhu M Z, Eckenhoff W T, Pintauer T, Jin R C. J Phys Chem C, 2008, 112: 14221
- 31 Zhu Y, Qian H F, Drake B A, Jin R C. Angew Chem, Int Ed, 2010, 49: 1295
- 32 Zhu Y, Wu Z K, Gayathri C, Qian H F, Gil R R, Jin R C. J Catal, 2010, 271: 155
- 33 Zhu Y, Qian H F, Jin R C. Chem Eur J, 2010, 16: 11455
- 34 Shichibu Y, Negishi Y, Watanabe T, Chaki N K, Kawaguchi H, Tsukuda T. *J Phys Chem C*, 2007, **111**: 7845
- 35 Qian H F, Zhu M Z, Lanni E, Zhu Y, Bier M E, Jin R C. J Phys

Chem C, 2009, 113: 17599

- 36 Zhu M, Aikens C M, Hendrich M P, Gupta R, Qian H, Schatz G C, Jin R C. J Am Chem Soc, 2009, 131: 2490
- 37 Deng Y H, Cai Y, Sun Z K, Liu J, Liu C, Wei J, Li W, Liu C, Wang Y, Zhao D Y. J Am Chem Soc, 2010, 132: 8466
- 38 Kumar S B, Mirajkar S P, Pais G C G, Kumar P, Kumar R. J Catal, 1995, 156: 163
- 39 Xu R, Wang D S, Zhang J T, Li Y D. Chem-Asian J, 2006, 1: 888
- 40 Liu J H, Wang F, Xu T, Gu Z G. Catal Lett, 2010, 134: 51
- 41 Patil N S, Uphade B S, Jana P, Bharagava S K, Choudhary V R. *J Catal*, 2004, **223**: 236
- 42 Yin D H, Qin L S, Liu J F, Li C Y, Jin Y. J Mol Catal A, 2005, 240: 40
- 43 Wu Z K, Jin R C. ACS Nano, 2009, 3: 2036
- 44 Jiang D E, Tiago M L, Luo W D, Dai S. *J Am Chem Soc*, 2008, 130: 2777
- 45 Jiang D E, Nobusada K, Luo W, Whetten R L. ACS Nano, 2009, 3: 2351