An atomic-level Catalysis of $Au_n(SR)_m$ Nanoclusters for Stereoselective Epoxidation of Stilbene

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Abstract   The efficient and stereoselective epoxidation of cis-stilbene and trans-stilbene was achieved at the atomic level using atomically precise $Au_n(SR)_m$ nanoclusters catalysts in mild conditions, involving thiolate-capped $Au_{25}(SR)_{18}$, $Au_{38}(SR)_{24}$, and $Au_{144}(SR)_{60}$ nanoclusters. These Au_n nanoclusters, which are ideally composed of an exact number of gold atoms, have unique atom packing structures and non-metallic electronic properties and show super catalysis comparing to current gold nanoparticles. The atomic-level understanding of mechanism is particularly interesting and the correlation of their structure and properties may provide us a deep insight into the fundamental nanogold catalysis.

Keywords Au_n Nanoclusters, Stereoselective Epoxidation, Atomic-Level Catalysis

1. Introduction

The new development of structurally well-defined catalytic systems that emulate nature's capacity to directly create stereochemical compounds is of great interest in the chemical synthesis era. Au nanoparticles have been proved to be a class of excellent catalysts for alkenes epoxidation implying propene, styrene, or cyclohexene epoxidation processes,[1] however, the development of efficient stereoselective epoxidation still presents a great challenge, despite the steric demands of epoxides from non-terminal alkenes are readily differentiated for pharmaceuticals, agrochemicals, and fine chemicals. Hughes et al. reported the formation of trans-epoxide and cis-epoxide from the selective oxidation of cis-stilbene on Au/C catalyst in the presence of TBHP, whereas its application is only restricted in a small-scale laboratory experiment process by the very low yield (5.5% in toluene as a solvent).[2] Additionally Lignier et al. found the high activity of Au/TiO_2 in the stereoselective epoxidation of trans-stilbene in methylcyclohexane as a solvent, however the mechanistic description was concentrated on the effect of methylcyclehexane in the free-radical reaction, and made no mention of the catalysis of gold catalyst on trans-stilbene epoxidation.[3] Recently we disclosed the effective epoxidation of styrene using atomically precise $Au_n(SR)_m$ nanoclusters as catalysts and proposed a understanding of the nanocatalysis of Au_n nanoclusters at atomic level, wherein each active site on Au_n surface conducts selective access to epoxidation. It is realized that the site-specific catalysis of

Au_n nanoclusters can be employed to transfer a variety of non-terminal alkenes for stereoselective epoxidation. Herein, we report the atomic level catalysis of Au_n nanoclusters for efficiently stereoselective epoxidation of cis-stilbene and trans-stilbene.

Such Au_n nanoclusters are composed of metal core with a precisely controlled, specific number of gold atoms, formulated as $Au_n(SR)_m$, where, n and m represent the respective numbers of gold atoms and thiolate ligands in the particle. Here, atomically monodisperse $Au_n(SR)_m$ nanoclusters (where R stands for $-CH_2CH_2Ph$), involving $Au_{25}(SR)_{18}$ (~1 nm in diameter), $Au_{38}(SR)_{24}$ (1.3 nm in diameter), and $Au_{144}(SR)_{60}$ (1.6 nm in diameter) were synthesized by wet chemistry approaches.[4-7]

2. Experimental

2.1. Synthesis of $Au_n(SR)_m$ catalysts (R= CH_2CH_2Ph)

$Au_{25}(SR)_{18}$ nanoclusters: $HAuCl_4 \cdot 3H_2O$ (0.4 mmol, dissolved in 5 ml nanopure water), and tetraoctylammonium bromide (TOAB, 0.47 mmol, dissolved in 10 ml toluene), were combined in a 25 ml tri-neck round bottom flask. The solution was vigorously stirred for 15 min, and the aqueous was then removed. The toluene solution of Au (III) was purged with N_2 and cooled down to 273 K in an ice bath over a period of 30 min under constant magnetic stirring. $PhCH_2CH_2SH$ (0.17 ml) was added to the flask, and stirring was reduced to a very low speed (~50 rpm). After the solution turns to clear (~ 1 hr), $NaBH_4$ (4 mmol, ~7 ml aqueous solution) was rapidly added all at once. The reaction was allowed to proceed overnight under N_2 atmosphere. After aging overnight, ethanol was added to separate Au_{25} clusters from TOAB and other side-products. The Au_{25} clusters

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were collected after removing the supernatant.

Au$_{38}$(SR)$_{24}$ nanoclusters: HAuCl$_4$·3H$_2$O (0.3 mmol) was first dissolved in methanol (20 mL) and phenylethanethiol (1.2 mmol, PhCH$_2$CH$_2$SH) was dissolved in nanopure water (10 mL). The two solutions were then mixed and then the mixture was cooled to ca. 273 K in an ice bath. NaBH$_4$ (3 mmol, dissolved in 6 mL nanopure water) was added to the suspension under vigorous stirring. After reaction for another hour, the resulting precipitation (Au:SR) was collected by centrifugation and washed with methanol. The above Au:SR clusters were dissolved in H$_2$O (4 mL). Then acetone (6 mL) and phenylethanethiol (8 mL) were added and the PhCH$_2$CH$_2$SH phase forms the upper layer and the aqueous solution of Au:SR clusters forms the bottom layer. The solution was heated to 353 K and allowed to react for several hours under vigorous stirring. After 3 h, the Au clusters were completely transferred to the organic phase. The isolated phenylethanethiol phase was washed thoroughly with excess ethanol and then with acetone to remove excess phenylethanethiol and byproducts. The major fraction containing Au$_{38}$ clusters was extracted with toluene from the crude product.

Au$_{144}$(SR)$_{60}$ nanoclusters: Toluene solution (20 mL) of TOAB (0.116 mmol) was mixed with an aqueous solution of HAuCl$_4$·3H$_2$O (0.1 mmol, 20 mL). After phase transfer of gold(III) into toluene, the aqueous layer was removed; PhCH$_2$CH$_2$SH (1.5 mmol) was added to the toluene solution, followed by stirring for 30 min. The mixture was then cooled to 0 °C. NaBH$_4$ (0.1 mmol, dissolved in 20 mL 0 °C nanopure water) was rapidly injected into the solution under vigorous stirring. After reaction overnight, the organic phase was washed thoroughly with water and then rota-evaporated to dryness. The residue was washed with methanol to remove excess PhCH$_2$CH$_2$SH, TOAB, and other byproducts. The dried samples (~20 mg) were incubated in pure PhCH$_2$CH$_2$SH at 80℃ for 24 hr under vigorous stirring. The final solution was washed thoroughly with methanol and then acetone to remove by-products such as gold(I): PhCH$_2$CH$_2$SH complexes. The Au$_{144}$(SCH$_2$CH$_2$Ph)$_{60}$ clusters were extracted from the products using a mixed toluene/acetone (1:1, v:v) solvent.

Supported Au$_n$ catalysts: The supported Au$_n$ catalysts were obtained by stirring a solution of Au$_n$(SR)$_m$ nanoclusters in dichloromethane with a calculated amount of SiO$_2$ for one day and then the solution was removed in flowing nitrogen. The synthesis of Au$_n$/CeO$_2$ is similar with that of Au$_n$/SiO$_2$.

2.2. Catalytic Test

Catalytic reaction was carried out at atmospheric pressure. Supported Au$_n$ catalysts (100 mg powder, 1%wt loading Au$_n$(SR)$_m$), stilbene (5 mmol), and TBHP (t-butyl hydroperoxide, 17 mmol) were added in a solvent (15 mL) in a 100 mL sealed glass reactor. Then the above mixture was heated to 82℃ under constant vigorous stirring in an oil bath for a certain reaction time. The solvent was removed with rota-

tion evaporation and the products were analyzed by ^{1}H NMR spectroscopy. The conversion and selectivity were calculated by quantitative NMR.

2.3. Characterization

^{1}H NMR spectra were measured at Bruker Avance^{TM} 300 MHz. UV-vis absorption spectra (190-1100 nm) were recorded using a Hewlett-Pachard (HP) 8453 diode array spectrophotometer. Electrospray ionization mass spectra were acquired using a Waters Q-TOF mass spectrometer equipped with Z-spray source.

3. Results and Discussion

These as-prepared Au$_n$ nanoclusters possess a non- crystallographic atom packing structures (Figure 1). In detail, the crystal structure of Au$_{25}$(SR)$_{18}$ nanocluster is arranged in six "V-shaped" –S(R)-Au-S(R)-Au-S(R)– staples, based on a centered icosahedral Au$_{13}$ kernel encapsulated by twelve gold atoms shell.[8,9] The entire particle adopts a quasi-D$_{2h}$ symmetry and is protected by 18 thiolate ligands. The crystal structure of Au$_{38}$(SR)$_{24}$ nanocluster is based on a face-fused biicosahedral Au$_{23}$ core which adopts a D_{3h} symmetry. The Au$_{23}$ core is structurally strengthened by three monomeric staples –S(R)-Au-S(R)– distributed at the waist of Au$_{23}$ and six dimeric staples –S(R)-Au-S(R)-Au-S(R)– evenly distributed on the two icosahedral units of Au$_{23}$ core.[10] The atom packing structure of Au$_{144}$(SR)$_{60}$ nanocluster is theoretically predicted to be arranged in –S(R)-Au-S(R)– staples with an icosahedral Au$_{114}$ core capped by 30 gold atoms shell.[11] Such precisely controlled Au$_n$ nanocatalysts offers unique opportunity for investigating nanocatalysis and the correlation of structure with their catalytic properties at the atomic level.
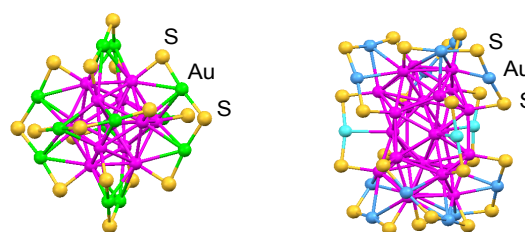

Figure 1. The crystal structures of Au$_{25}$ and Au$_{38}$ nanoclusters. (for clarity, only Au and S atoms were shown)

The stereoselective epoxidation of cis-stilbene and trans-stilbene was chosen as a target to evaluate the selectivity and activity of Au$_n$(SR)$_m$ nanoclusters catalysts, where, TBHP is used as an effective oxidant for epoxidation of olefins. Considering for the commercial interest, such as reuse of catalysts or easy-separation from reaction system, supported Au$_n$(SR)$_m$ nanocatalysts are investigated on inert silica and non-inert metal oxides, respectively. Cis-stilbene and trans-stilbene as aromatic non-terminal alkenes are not apt to be oxidized compared with terminal alkenes. In the absence of TBHP, no stilbene conversion was observed,

when the experiment was carried out using O$_2$ as an oxidant. In the presence of TBHP, no epoxide products were found without gold catalyst. This indicates that hydroperoxide and gold catalyst are necessary for stilbene epoxidation.

Firstly, Au$_n$(SR)$_m$/SiO$_2$ catalysts were investigated which is based on the indeed identification of gold active species without reference from the interaction of Au$_n$ and supports. Table 1 shows the catalytic performance of Au$_n$(SR)$_m$/SiO$_2$ catalysts for stereoselective epoxidation of cis-stilbene. With Au$_{25}$(SR)$_{18}$/SiO$_2$ catalyst, the selectivity of trans-epoxide up to 98% was observed at 26% conversion of cis-stilbene. The other products, cis-stilbene epoxide and benzaldehyde, have only negligible amounts(~1% selectivities for both). Au$_{38}$(SR)$_{24}$/SiO$_2$ catalyst achieved near 100% selectivity to trans-epoxide and 15% conversion of cis-stilbene, and Au$_{144}$(SR)$_{60}$/SiO$_2$ catalyst gave rise to 14% conversion of cis-stilbene and 91% selectivity to trans-epoxide, 2% selectivity to cis-stilbene epoxide and 7% selectivity to benzaldehyde. In Table 1, the catalytic results of Au$_n$/CeO$_2$ show that the conversion of cis-stilene is efficiently promoted by the supported Au$_n$ on CeO$_2$ catalysts. Noted Only CeO$_2$ support can not convert stilbene. Au$_{25}$/CeO$_2$ catalyst achieved 54% conversion of cis-stilbene and 96% selectivity of trans-stilbene epoxide. Au$_{38}$/CeO$_2$ catalyst gave rise to 48% conversion with 97% selectivity of trans-stilbene epoxide. Au$_{144}$/CeO$_2$ catalyst converted 49% cis-stilbene with 97% selectivity toward trans-stilbene epoxide. Test results indicated the important role that CeO$_2$ support can play cooperating in the activity of suported gold.[12,13] Interestingly, CeO$_2$ support has no obvious effect on the selectivity of cis-stilbene epoxidation.

With respect to the stereoselective epoxidation of trans-stilbene on supported Au$_n$ catalysts, trans-stilbene epoxide is a major product, benzaldehyde is a second product and cis-stilbene epoxide is a minor product. All these Au$_n$ catalysts exhibited a higher activity for trans-stilbene oxidation that they converted more amount of trans-stilbene comparing to cis-stilbene system (Table 2). As Au$_n$ were supported on SiO$_2$, 51% conversion with 94% selectivity of trans-stilbene epoxide was obtained on Au$_{25}$; 43% conversion with 93% selectivity of trans-stilbene epoxide was achieved on Au$_{38}$; 36% conversion with 93% selectivity of trans-stilbene ep-

oxide was obtained on Au$_{144}$. Au$_n$/CeO$_2$ promoted the trans-stilbene oxidation: Au$_{25}$ catalyzed trans-stilbene into trans-stilbene epoxide in 95% selectivity at 83% conversion; Au$_{38}$ gave 95% of trans-stilbene epoxide at 81% conversion; Au$_{144}$ achieved 95% selectivity toward trans-stilbene epoxide at 76% conversion.

Table 1. Catalytic results of cis-stilbene epoxidation with supported Au$_n$ nanoclusters as catalysts. (100 mg catalysts, 1%wt Au$_n$(SR)$_m$ loading, 5 mmol cis-stilbene, 17 mmol TBHP, 15 mL CH$_3$CN as solvent, 82℃, 24 hr.)
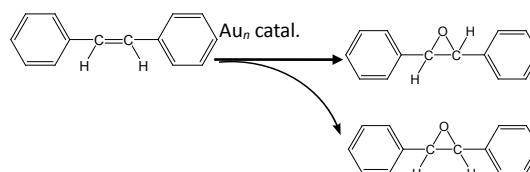
Catalysts	Conversion	Selectivity (%)		
	(%)	trans-epoxide	cis-epoxide	benzaldehyde
Au$_{25}$/SiO$_2$	26	98	1	1
Au$_{38}$/SiO$_2$	15	100	0	0
Au$_{144}$/SiO$_2$	14	91	2	7
Au$_{25}$/CeO$_2$	54	96	2	2
Au$_{38}$/CeO$_2$	48	97	1	2
Au$_{144}$/CeO$_2$	49	97	2	1

Table 2. Catalytic results of trans-stilbene epoxidation catalyzed by supported Au$_n$ catalysts. (100 mg catalysts, 1%wt Au$_n$(SR)$_m$ loading, 5 mmol trans-stilbene, 17 mmol TBHP, 15 mL CH$_3$CN as solvent, 82 ℃, 24 hr.)
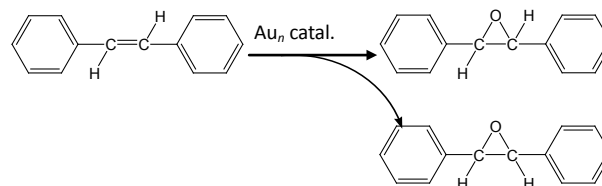
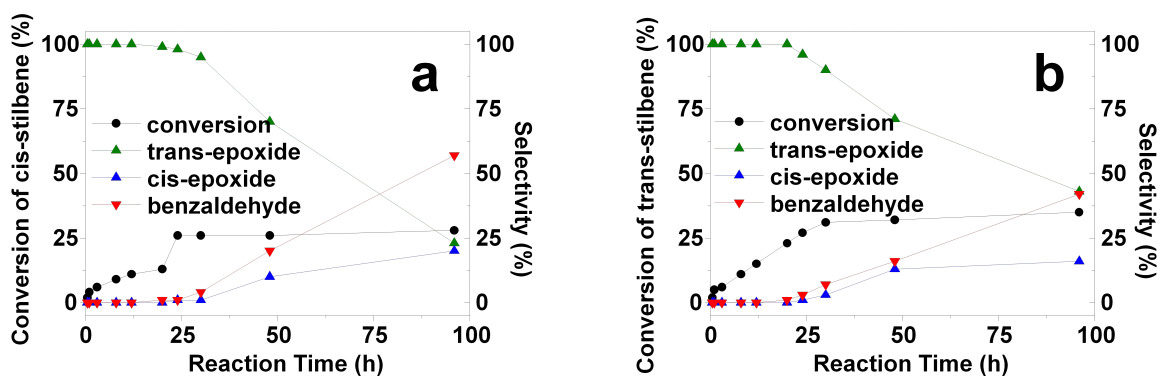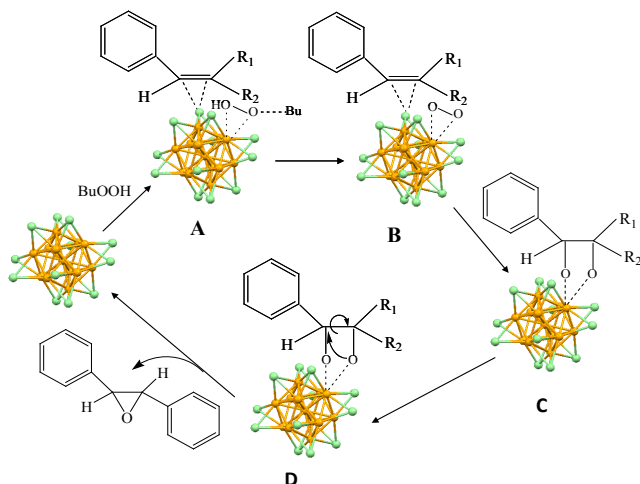| Catalysts	Conversion	Selectivity (%)		
	(%)	trans-epoxide	cis-epoxide	benzaldehyde
Au$_{25}$/SiO$_2$	51	94	trace	6
Au$_{38}$/SiO$_2$	43	93	trace	7
Au$_{144}$/SiO$_2$	36	93	trace	7
Au$_{25}$/CeO$_2$	83	95	1	4
Au$_{38}$/CeO$_2$	81	95	1	4
Au$_{144}$/CeO$_2$	76	95	1	4

Figure 2. The conversions and selectivities of (a) cis-stilbene and (b) trans-stilbene epoxidation on Au$_{25}$/SiO$_2$ catalyst at different reaction time, respectively

Scheme 1. Proposed mechanism of the stereoselective epoxidation of stilbene on site-specific catalysis of Au_{25} nanocluster. Golden: Au atoms of the core; blue: Au atoms of the shell. (Where, when R_1 is phene and R_2 is H, the reagent is cis-stilbene; when R_1 is H and R_2 is phene, the reagent is trans-stilbene.)

Moreover, the kinetic study of the reaction profile and reaction time suggested the rate of trans-epoxide formation is much higher than that of cis-epoxide due to the sterical hindrance and potential-energy barriers (Figure 2). At the beginning, the formation of trans-stilbene epoxide is earlier than other products. With the reaction time, the worm increase of cis-stilbene epoxide selectivity indicates a rotation about the C−C bond following the formation the two C−O bonds of trans-stilbene epoxide. The formation of benzaldehyde results from the sequential oxidation at high temperature. When the reaction time is longer (>30 h), the increase in the benzaldehyde selectivity and decrease in the epoxide with increasing the reaction time are caused by the overoxidation of C=C double bond of stilbene at high temperature. Over 25 h reaction time, the conversion of stilbenes, including cis-stilbene and trans-stilbene, has no significant increase, indicating that a reaction equilibrium is reached. The specific activity of Au_n nanoclusters can be explained by their core-shell-type geometrical and electronic structures. Scheme 1 presents a proposed mechanism for epoxidation of stilbene catalyzed by Au_{25} nanocluster. In the first step, the free radical process involving the interaction of TBHP and electron-rich Au_{13} core generates a hydroperoxy species A, and then species A undergoes one-electron reduction with a loss of H_2O molecule and rearranges to give rise to the peroxo intermediate species B (Au_{25}−O−O). Meanwhile, the presence of partial positive charges on the surface gold atoms ($Au^{\delta+}$, $0<\delta<1$) of the Au_{12} shell, that is electrophilic Au atoms on the shell, should be responsible to active the nucleophilic C=C double bond of stilbene (species B). Then the peroxidic oxygen is unstable and labile to attack the activated nucleophilic C−C bond through side-by-side interaction on Au_{25} surface sites, in which a transient species C is formed. When reagent is trans-stilbene (where R_1 is H and R_2 is phene), trans-epoxide is formed through the transformation of one oxygene to C−C bond and the remove of the other

oxygene from species D. When reagent is cis-stilbene, that is, R_1 is phene and R_2 is H, stereoselectivity of trans-epoxide and cis-epoxide is controlled through the difference in the potential-energy barriers of single reaction channel.[14] While one oxygene transfer to olefinic band, R_1−C−R_2 group rotates around the C−C bond since the activation energies of trans-epoxide and cis-epoxide makes the trans-epoxide channel become favored. Therefore, the trans-epoxide product is preferable to form and then Au_{25} returns to active starting-point for another cycle to trigger the catalytic reaction.

4. Conclusions

In summary, we have developed a highly efficient stereoseletive epoxidation of stilbene using atomically precise Au_n nanoclusters catalysts at an atomic level. The site-specific activity of Au_n nanoclusters is attributed to their core-shell-type geometrical and electronic structures. The site-specific catalysis of Au_n nanoclusters is promising to develop reaction classes that are widely viewed as important within the field of stereoselective catalysis.

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