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# Atomic level tuning of the catalytic properties: Doping effects of 25-atom bimetallic nanoclusters on styrene oxidation

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## ABSTRACT

Atomically precise bimetallic  $M_xAu_{25-x}(SR)_{18}$  ( $M=Cu$  and  $Ag$ ,  $R=CH_2CH_2Ph$ ) nanoclusters are investigated as oxide-supported catalysts for the catalytic oxidation of styrene. Their catalytic properties are compared with the case of homogold  $Au_{25}(SR)_{18}$  nanocluster. The oxide-supported  $M_xAu_{25-x}(SR)_{18}$  catalysts give rise to 42–82% conversion of styrene at 70 °C using (diacetoxyiodo)benzene ( $PhI(OAc)_2$ ) as the oxidant. The  $Ag$  and  $Cu$  dopants are found to modulate both the activity (i.e., conversion of styrene) and the selectivity to styrene epoxide or benzaldehyde (major products). The  $Ag_xAu_{25-x}(SR)_{18}$  clusters exhibit higher activity and benzaldehyde selectivity than the homogold cluster, while the  $Cu_xAu_{25-x}(SR)_{18}$  clusters primarily enhance the selectivity to benzaldehyde without significantly changing the activity. The results provide insights into the factors that influence the catalytic activity and selectivity in styrene oxidation.

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## 1. Introduction

Gold-based bimetallic nanocluster catalysts as well as homogold nanoclusters hold potential in a variety of reactions [1–4], such as catalytic oxidation reactions of CO [5,6], alcohols [7–9], and olefins [10–13] (e.g., propene and styrene). Recent advances in the synthesis of ligand-protected nanoclusters in solution phase have achieved atomic level control of the composition of gold-based bimetallic nanoclusters [14]. A notable example is the attainment of bimetallic  $M_xAu_{25-x}(SR)_{18}$  nanoclusters ( $M=Ag$  and  $Cu$ ) [15–17]. Although their structure is similar to that of the homogold  $Au_{25}(SR)_{18}$  nanocluster, the bimetallic nanoclusters exhibit different electronic properties due to the substitution of heteroatoms into the gold framework [14–17]. Such effects prompt us that the catalytic properties of bimetallic  $M_xAu_{25-x}(SR)_{18}$  would also be changed compared to the  $Au_{25}(SR)_{18}$  nanocluster, albeit all of these clusters share the same atomic packing structure.

Previously Xie et al. reported that the ligand-off  $Pd_1Au_{24}$  nanoclusters on multiwalled carbon nanotubes gave rise to a much better catalytic activity than that of the ligand-off  $Au_{25}$  nanocluster in aerobic oxidation of benzyl alcohol to benzaldehyde [18]. Selective oxidation of organic compounds (e.g., alcohol and olefins)

with environmentally friendly oxidants (e.g., oxygen, hydrogen peroxide, and (diacetoxyiodo)benzene) is an important direction in green organic catalytic chemistry [19,20]. Murakami et al. reported epoxidation of olefins catalyzed by a manganese–porphyrin complex with dodecanethiolate-protected metallic gold nanoclusters as a co-catalyst and iodosylbenzene ( $PhIO$ ) as the oxidant [21]. In our previous work, we investigated the catalytic properties of monoplatinum-doped  $Pt_1Au_{24}(SR)_{18}/TiO_2$  using  $PhI(OAc)_2$  as oxidant in the oxidation of styrene [22]. The  $Pt$ -centered  $Pt_1Au_{24}(SR)_{18}$  cluster showed much higher catalytic activity and selectivity for benzaldehyde than the  $Au_{25}(SR)_{18}$  cluster catalyst.

Herein, we are motivated to investigate the catalytic properties of copper and silver-doped nanoclusters. Compared to the monodoping cases of  $Pd$  and  $Pt$  [23,24], the dopants of  $Cu$  and  $Ag$  typically produce a range of the dopant numbers in  $M_xAu_{25-x}(SR)_{18}$  nanoclusters [15–17], but the total number of metal atoms is retained at 25.

In this work we investigate the catalytic activities of the gold-based bimetallic  $M_xAu_{25-x}(SR)_{18}$  nanoclusters (where,  $M=Ag$  and  $Cu$ ) in the oxidation of styrene using (diacetoxyiodo) benzene ( $PhI(OAc)_2$ ) as the oxygen source. The  $PhI(OAc)_2$  oxidant is of low toxicity and is a very powerful oxygen atom donor in epoxidation reactions [25].

## 2. Experimental

2.1 Synthesis and characterization of  $M_xAu_{25-x}(SR)_{18}$  ( $M=Cu$ ,  $Ag$ ) and  $Au_{25}(SR)_{18}$

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$\text{Cu}_x\text{Au}_{25-x}(\text{SC}_2\text{H}_4\text{Ph})_{18}$ ,  $\text{Ag}_x\text{Au}_{25-x}(\text{SC}_2\text{H}_4\text{Ph})_{18}$ , and  $\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}$  were synthesized according to modified methods [17,26]. The synthesis of  $\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}$  is as follows. Tetraoctylammonium bromide (TOABr, 101.5 mg) and  $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$  (60.9 mg) were dissolved in THF (10 mL) in a three-necked flask.  $\text{PhCH}_2\text{CH}_2\text{SH}$  (106 mL) was slowly added to the flask. After the solution turned clear over a period of ca. 0.5 h, an aqueous solution of  $\text{NaBH}_4$  (58.7 mg, freshly dissolved in 3 mL ice-cold nanopure water) was rapidly added at once under slow stirring. After ca. three hours, the reaction was stopped, and THF was removed by rotary evaporation. The black solids were collected and thoroughly washed with MeOH,  $\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}$  was extracted by MeCN, and characterized by matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) analysis. The syntheses of  $\text{Cu}_x\text{Au}_{25-x}(\text{SC}_2\text{H}_4\text{Ph})_{18}$  and  $\text{Ag}_x\text{Au}_{25-x}(\text{SC}_2\text{H}_4\text{Ph})_{18}$  nanoclusters followed a similar procedure as above, except that copper(II) acetate and silver(I) acetate were added in a 1–10 copper-to-gold and silver-to-gold ratio.

## 2.2. Characterization of cluster

The UV–vis spectra of the nanoclusters (dissolved in  $\text{CH}_2\text{Cl}_2$ ) were acquired on a Hewlett–Packard (HP) Agilent 8453 diode array spectrophotometer at room temperature. Matrix-assisted laser desorption/ionization (MALDI) mass spectrometry was performed with a PerSeptive Biosystems Voyager DE super-STR time-of-flight (TOF) mass spectrometer. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenyldiene]-malononitrile (DCTB) was used as the matrix in MALDI-MS analysis. Typically, 0.1 mg matrix and 10  $\mu\text{L}$  analyte stock solution were mixed in 10  $\mu\text{L}$   $\text{CH}_2\text{Cl}_2$ , and the mixed solution was applied to the steel plate and then air-dried prior to MALDI analysis.

## 2.3. Preparation of 1 wt% $\text{M}_x\text{Au}_{25-x}(\text{SR})_{18}$ /oxides ( $\text{M}=\text{Cu}, \text{Ag}$ ) and 1 wt% $\text{Au}_{25}(\text{SR})_{18}$ /oxides

Typically, 1 mg  $\text{M}_x\text{Au}_{25-x}(\text{SR})_{18}$  or  $\text{Au}_{25}(\text{SR})_{18}$  clusters were dissolved in 5 mL DCM, and 100 mg oxides ( $\text{TiO}_2$ ,  $\text{CeO}_2$  and  $\text{SiO}_2$ ) were added. After stirred 12 h at r.t.,  $\text{M}_x\text{Au}_{25-x}(\text{SR})_{18}$ /oxides catalysts were collected by centrifugation and dried in vacuum. As shown in the high-resolution scanning transmission electron microscopy (STEM) image, the interplanar distance of the  $\text{TiO}_2$  support is 0.35 nm (Fig. S1 in the Supporting information), in agreement with the {1 0 1} plane of the anatase phase of  $\text{TiO}_2$ .

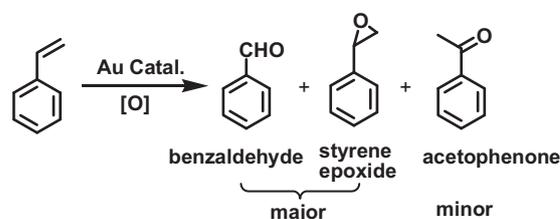
## 2.4. Typical procedure for styrene oxidation

In a typical reaction,  $\text{Ph}(\text{OAc})_2$  (0.1 mmol), styrene (0.1 mmol) and 1 wt% cluster/oxide catalysts (100 mg, pretreated at 150 °C in vacuum for 2 h) were mixed in 2 mL acetonitrile. The mixture was stirred under  $\text{N}_2$  atmosphere at 70 °C for 10 h as indicated in Table 1. The product was obtained after removal of the solvent of the supernatant. The conversion of styrene and yields of styrene epoxide, benzaldehyde and acetophenone were determined by  $^1\text{H}$  NMR (300 MHz) spectroscopic analysis.

## 3. Results and discussion

### 3.1. Characterization of clusters

The three types of nanoclusters i.e., multiple-atom doped  $\text{Cu}_x\text{Au}_{25-x}(\text{SR})_{18}$  ( $x=0-5$ ) and  $\text{Ag}_x\text{Au}_{25-x}(\text{SR})_{18}$  ( $x=4-8$ ) [17], as well as homogold  $\text{Au}_{25}(\text{SR})_{18}$  nanoclusters [26] were synthesized following the literature protocols. The nanoclusters were characterized by matrix-assisted laser desorption/ionization (MALDI) mass spectrum (Fig. 1). The MALDI mass spectrum of  $\text{Au}_{25}(\text{SR})_{18}$



**Scheme 1.** Oxidation of styrene to yield styrene epoxide, benzaldehyde, and acetophenone.

nanocluster exhibits a single intense peak at  $m/z$  7394 ( $z=1$ ), consistent with the calculated formula weight of 7393.72 for  $\text{Au}_{25}(\text{SR})_{18}$ , where  $\text{R}=\text{CH}_2\text{CH}_2\text{Ph}$  (Fig. 1B); of note, the small peak at 6057 is an inevitable fragment ( $\text{Au}_{21}(\text{SR})_{14}$ ) caused by the somewhat destructive MALDI method, i.e., laser irradiation caused the loss of a  $\text{Au}_4(\text{SR})_4$  unit from the parent  $\text{Au}_{25}(\text{SR})_{18}$  nanocluster, resulting in some  $\text{Au}_{21}(\text{SR})_{14}$  fragments [26]. No other peaks were found, indicating the high purity of the  $\text{Au}_{25}(\text{SR})_{18}$  nanoclusters. The cases of Ag and Cu doping gave rise to a range of  $x$  values for  $\text{Ag}_x\text{Au}_{25-x}(\text{SR})_{18}$  or  $\text{Cu}_x\text{Au}_{25-x}(\text{SR})_{18}$  (Fig. 1C and D), but the total number of metal atoms per cluster is preserved at 25, indicating the high stability of the 25-metal-atom structure [13]. As shown in Fig. 1C, the average spacing of the  $\text{Ag}_x\text{Au}_{25-x}(\text{SR})_{18}$  peaks is 89.5, i.e., the atomic mass difference between gold and silver ( $M_{\text{Au}}-M_{\text{Ag}}=197.0-107.9=89.1$ ), which suggests that gold atoms are successively replaced by silver atoms with the total number retained at 25. Similarly, in the case of  $\text{Cu}_x\text{Au}_{25-x}(\text{SR})_{18}$  (Fig. 1D), the average peak spacing is 133.8 (theoretical  $M_{\text{Au}}-M_{\text{Cu}}=197.0-63.5=133.5$ ), which also indicates the substitution of copper for gold atoms; however, the maximum replacement in  $\text{Cu}_x\text{Au}_{25-x}(\text{SR})_{18}$  is only up to  $x=5$  and is less than the case of  $\text{Ag}_x\text{Au}_{25-x}(\text{SR})_{18}$  (where,  $x$  up to 8), Fig. 1C and D (insets).

### 3.2. Catalytic properties of $\text{M}_x\text{Au}_{25-x}(\text{SR})_{18}$ ( $\text{M}=\text{Cu}, \text{Ag}$ ) and $\text{Au}_{25}(\text{SR})_{18}$ clusters

The  $\text{M}_x\text{Au}_{25-x}(\text{SR})_{18}$  ( $\text{M}=\text{Cu}, \text{Ag}$ ) and  $\text{Au}_{25}(\text{SR})_{18}$  clusters were supported onto inorganic oxides (e.g.,  $\text{TiO}_2$ ,  $\text{SiO}_2$ , and  $\text{CeO}_2$ ) by impregnation of oxide powders in a dichloromethane (DCM) solution of clusters. The catalytic oxidation of styrene was performed in acetonitrile at 70 °C for 10 h under a  $\text{N}_2$  atmosphere, and other conditions are as follows: 0.1 mmol styrene, 0.1 mmol  $\text{Ph}(\text{OAc})_2$ , 100 mg of  $\text{M}_x\text{Au}_{25-x}(\text{SR})_{18}$ /oxides (1 wt% loading of ligated clusters). The conversion of styrene and the selectivities for benzaldehyde, styrene epoxide, and acetophenone were analyzed by  $^1\text{H}$  NMR. In general, three products (styrene epoxide, benzaldehyde, and acetophenone) were yielded during the catalytic oxidation of styrene by gold nanoclusters (Scheme 1) [27–29]. A typical  $^1\text{H}$  NMR spectrum is shown in Fig. S2. NMR analysis identified four components in the crude product: the residual styrene which shows signals at  $\delta=\sim 5.25, 5.75$  ppm ( $-\text{C}=\text{CH}_2$ ), and 6.75 ppm ( $\text{Ph}-\text{HC}=\text{CH}_2$ ), styrene epoxide at  $\sim 2.83, 3.18$  ppm ( $\text{PhCHOCH}_2$ ) and 3.87 ppm ( $\text{PhCHOCH}_2$ ), benzaldehyde at 10.02 ppm ( $\text{Ph}-\text{CHO}$ ) and acetophenone at 2.56 ppm ( $\text{PhCOCH}_3$ ). The phenyl groups of the four compounds and another side-product iodobenzene were overlapped from 7.0 to 8.2 ppm. The integrated peak areas and the  $J$ – $J$  coupling constants confirm the above assignment. By integrating and normalizing the NMR peak areas, the conversion and selectivity are calculated (averaged over three runs).

We first compare the three types of clusters supported on  $\text{TiO}_2$ . As shown in Table 1 (entries 1–4), the blank test (i.e., using plain  $\text{TiO}_2$  in the catalytic reaction) showed a 15.8% conversion of styrene, while the  $\text{Au}_{25}(\text{SR})_{18}/\text{TiO}_2$  catalyst showed a much higher conversion of styrene (58.9%), indicating that gold clusters are

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