



Au₂₅ clusters as precursors for the synthesis of AuPd bimetallic nanoparticles with isolated atomic Pd-surface sites

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ABSTRACT

This study documents the synthesis of Al₂O₃-supported AuPd bimetallic nanoparticles with isolated atomic Pd-surface sites using Au₂₅(SC₈H₉)₁₈ clusters as starting precursors. Here, previously synthesized thiolate protected AuPd bimetallic clusters were supported on Al₂O₃ and subjected to thermal and LiBH₄ treatments. Extended X-ray absorption fine structure (EXAFS) analysis shows that thermal and LiBH₄ treatments of Al₂O₃ supported AuPd bimetallic clusters result in the formation of AuPd/Al₂O₃ bimetallic nanoparticles with isolated atomic Pd-surface sites. EXAFS data also shows that Pd atoms present on the surface were still bonded with thiolate stabilizers. Finally, AuPd/Al₂O₃ catalysts were tested for the hydrogenation of allyl alcohol. Data show that while Au₂₅/Al₂O₃ materials were inactive for the hydrogenation reaction, Al₂O₃ supported AuPd bimetallic clusters were catalytically active. The catalytic activity was further enhanced after thermal and LiBH₄ treatment and this was attributed to the enhanced access of substrates to surface Pd sites.

1. Introduction

Bulk Au had long been considered inactive for catalysis until the seminal discovery by Haruta et al. in 1987 showing that oxide supported, well-dispersed Au nanoparticles (less than 5 nm in size) can act as catalysts for low temperature CO oxidation reactions [1]. Since then, a plethora of research articles have been published showing the catalytic activity of supported Au nanoparticles for a wide range of reactions, such as oxidation of alcohols and alkenes, hydrogenation of alkenes and nitroaromatics, and the chemoselective hydrogenation of unsaturated aldehydes and ketones [2–9]. Various groups have shown that alloying Au with Pd leads to a significant enhancement in the catalytic activity and selectivity for various industrially important reactions, such as the oxidation of primary C–H bonds, direct H₂O₂ synthesis from hydrogen and oxygen, vinyl acetate synthesis, and the selective oxidation of alcohols [10–14]. The catalytic activity and selectivity of these AuPd bimetallic nanoparticles can be attributed to two main factors: 1) modulation in electronic structure upon mixing two metal components [15–18], and 2) a dilution effect; leading to the formation of catalytically active, isolated atomic Pd-surface sites on AuPd bimetallic nanoparticles [19–22]. While the effect of modulation in the electronic structure has been very well explored, very little research has been reported on the effect of isolated atomic Pd-surface sites of AuPd bimetallic nanoparticles towards catalytic activity and

selectivity. This is apparently because of the lack of facile synthetic methodologies available for the design of AuPd bimetallic nanoparticles with isolated atomic Pd-surface sites. The importance of having catalytically active isolated atomic Pd sites has been discussed by several groups [19–28]. For example, Goodman and co-workers have shown that the pair of isolated Pd sites were essential for the acetoxylation of ethylene resulting in the formation of vinyl acetate. Here, the role of two suitably spaced Pd-sites was to facilitate the coupling between surface acetate and ethylene species and to suppress the formation of undesirable reaction by products [19]. Sykes and co-workers have shown that isolated atomic Pd sites on Cu (111) surfaces enhances the selectivity of styrene and acetylene hydrogenation reactions towards ethyl benzene and ethane respectively by inhibiting the decomposition of these substrates [20]. Meyer and co-workers have shown that the isolation of active surface Pd atoms on inactive Zn cores was responsible for the exclusive dehydrogenation of propane to propylene, and indicated that the competing hydrogenolysis of propane did not take place because the latter reaction requires a contiguous Pd surface [21]. Zhang et al. demonstrated the synthesis of Au alloyed Pd single-atom catalyst with an ion exchange-NaBH₄ reduction method and showed that the resulting catalyst exhibited exceptional activity and durability for Ullman reactions of aryl halides [22]. Tsukuda and co-workers examined the catalytic activity of Pd₁Au₂₄(SC₁₂H₂₄)₁₈ clusters for benzyl alcohol oxidation reactions [23]. The catalytic data revealed

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a significant enhancement in the conversion (74%) during benzyl alcohol oxidation reaction using carbon nanotube-supported bimetallic catalysts activated at 450 °C, compared to the $\text{Au}_{25}(\text{SC}_{12}\text{H}_{24})_{18}$ clusters activated at the same temperature which showed only 22% conversion [23]. Later, the same group reported the synthesis of PVP protected PdAu_{33} and PdAu_{43} clusters, which were characterized using MALDI-MS and EXAFS and employed as catalysts for the aerobic oxidation of benzyl alcohol, and the chemoselective hydrogenation of cinnamyl alcohol [24]. Higher conversions were seen for oxidation reactions, which was attributed to the charge transfer from Pd to Au, and higher activity and selectivity was observed towards C–C bond hydrogenation during cinnamyl alcohol hydrogenation, due to the presence of segregated Pd atoms on the surface [24].

Atomically-precise, thiolate-protected Au clusters have recently emerged as an important class of materials because of their monodispersity and well-defined structures [29]. These clusters have been used by a number of groups in order to synthesize supported Au catalysts. Both ourselves and others have shown that supported Au clusters can be activated for a number of catalytic reactions by removing thiol stabilizers from the surface either thermally or chemically using BH_4^- reducing agents [30–32]. For example; we previously reported that mesoporous carbon supported $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}^-$ clusters can be activated for p-nitrophenol reduction catalysis by removing thiol stabilizers at ca. 200 °C [30]. Thermal treatments beyond 200 °C led to significantly lower catalyst activity because of sintering. Wu et al. reported that CeO_2 -supported $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}^-$ clusters can be activated for CO oxidation catalysis by thermally removing thiol stabilizers from the interface between CeO_2 and Au clusters at ca. 250 °C [31]. Das et al. reported the activation of SBA-15 supported $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}^-$ clusters using BH_4^- reducing agent for styrene oxidation reactions [32]. BH_4^- can reductively eliminate thiol stabilizers from the surface of monolayer protected Au clusters and therefore open-up the catalytically active sites [33,34].

A few groups have shown experimentally and theoretically that the co-precipitation methodology can be used to synthesize $\text{Pd}_1\text{Au}_{24}(\text{SR})_{18}$ bimetallic clusters. The structure of this bimetallic cluster can be viewed as the replacement of one Au atom by one Pd at the center of Au_{13} icosahedron core of Au_{25} cluster [35–37]. For example, Negishi et al. synthesized $\text{Pd}_1\text{Au}_{24}(\text{SC}_{12}\text{H}_{25})_{18}$ clusters using co-precipitation methodology, and revealed using MS and DFT calculations that the central Au atom of $\text{Au}_{25}(\text{SR})_{18}$ clusters gets replaced by one Pd atom, forming $\text{Pd}_1\text{Au}_{24}(\text{SC}_{12}\text{H}_{25})_{18}$ bimetallic clusters [35]. Subsequently, other groups also supported the formation of this core-shell type structure using Mössbauer spectroscopy, EXAFS spectroscopy, and single crystal X-ray diffraction [36,37]. However, post-synthetic treatment of $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}$ clusters with Pd(II) can result in the substitution of staple Au(I) species by Pd; we found using XAS, TEM, and UV–vis that Pd(II) salts react with $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}^-$ clusters through surface staple motifs to form Pd(II) thiolate species [38]. These Pd(II) thiolate species were found to be anchored on the surface of these clusters leading to the formation of thiolate protected AuPd bimetallic clusters. Later, theoretical simulation of the experimental XANES data of thiolate-protected AuPd bimetallic clusters, prepared by post-synthetic treatment also supported the presence of Pd in the staple motifs, although some Pd atoms were also found to be present inside the core [39]. This present study is an extension of our previous work. Here, using extended X-ray absorption fine structure (EXAFS) spectroscopy, we show that the thermal and LiBH_4 treatments of these thiolate-protected AuPd bimetallic clusters supported on Al_2O_3 leads to the formation of AuPd bimetallic nanoparticles with isolated atomic Pd-surface sites. Our data shows that surface Pd atoms are still bonded with thiolate stabilizers, which may partially constrain the growth of these bimetallic alloy nanoparticles during thermal and LiBH_4 treatments. The salient features of the present study are as follows: 1) since we are starting with highly monodisperse $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}^-$ clusters as starting precursors, better control over the final AuPd nanoparticle

compositions can be obtained, and 2) the ability to tune the number of catalytically active atomic Pd-surface sites of AuPd bimetallic nanoparticles can be achieved by simply varying the Au_{25} to Pd(II) ratio during bimetallic cluster synthesis.

2. Experimental

2.1. Materials

Hydrogen tetrachloroaurate(III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.9% on metal basis, Alfa Aesar), tetraoctylammonium bromide (TOAB, 98%, Aldrich), 2-phenylethanethiol ($\text{C}_8\text{H}_{10}\text{S}$, 99%, Acros Organics), sodium borohydride (NaBH_4 , 98%, EMD), palladium(II) acetate, trimer (99.98% on metal basis, Alfa Aesar), aluminum oxide (Al_2O_3 , 58 Å, ~150 mesh), LiBH_4 (1 M in THF, Sigma Aldrich), and deuterated chloroform (CDCl_3 , D-99.8%, Cambridge Isotope Laboratories) were used as received. High purity acetonitrile (HPLC grade, submicron filtered) and methanol (HPLC, 0.2 µm filtered) were purchased from Fischer Scientific. High purity tetrahydrofuran was purchased from EMD (HPLC grade) and 100% ethanol was purchased from Commercial Alcohols. 18 MΩ cm Milli-Q (Millipore, Bedford, MA) deionized water was used throughout.

2.2. Synthesis of $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}^-$ clusters

The synthesis of $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}^-$ clusters is reported elsewhere [40]. Briefly, 500 mg of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ in 50 mL of THF was mixed with 1.2 equiv. of TOAB. To this solution, 5 equiv. of 2-phenylethanethiol was added dropwise and the mixture was left for stirring until it became clear. Subsequently, 10 equiv. of NaBH_4 in 10 mL of ice cold water was added all at once. The resulting solution was stirred for 4 days. After 4 days, the reaction was stopped and the solvent was evaporated completely. The resulting solid was then washed with a mixture of ethanol/water several times to remove excess leftover thiol, and finally the residue was dried using a rotary evaporator. The resulting $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}^-$ clusters were extracted with acetonitrile and analyzed using UV–vis spectroscopy.

2.3. Sample preparation for EXAFS measurements

The $\text{Au}_{25}\text{Pd}_{0.5}$ sample was prepared by mixing 8 mg of $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}^-$ clusters with 0.5 equiv. of Pd acetate in THF and stirring the resulting solution overnight. The clusters were then immobilized on 100 mg of an Al_2O_3 support using a wetness impregnation approach and the obtained solid was dried by purging the sample using N_2 gas. Thermal treatment of the $\text{Au}_{25}\text{Pd}_{0.5}$ sample was done by calcining the obtained powder at 250 °C for 90 min first under air followed by 90 min of thermal treatment under H_2 atmosphere at 250 °C. LiBH_4 treatment of the $\text{Au}_{25}\text{Pd}_{0.5}$ sample was done by adding 0.1 mL of LiBH_4 (1.0 M in THF) dropwise to the 100 mg of the $\text{Au}_{25}\text{Pd}_{0.5}$ sample suspended in hexane. The resulting solution was stirred for 10 min and subsequently washed with hexane and dried by purging the resulting solid using N_2 gas. The $\text{Au}_{25}\text{Pd}_6$ sample was similarly prepared by mixing 13 mg of Au_{25} clusters with 6 equiv. of Pd acetate in THF and stirring the resulting solution overnight. Thermal and LiBH_4 treatments of the $\text{Au}_{25}\text{Pd}_6$ sample were done exactly in the same manner as done for the $\text{Au}_{25}\text{Pd}_{0.5}$ sample.

2.4. EXAFS measurements and analysis

EXAFS measurements were conducted at the Hard X-ray MicroAnalysis (HXMA) beamline 061D-1 (energy range 5–30 keV; resolution, 1×10^{-4} ΔE/E) of the Canadian Light Source (CLS, 2.9 GeV storage ring, 250 mA current). Samples were pressed into pellets and measured in transmission (the $\text{Au}_{25}\text{Pd}_6$ sample, Au L_{3} -edge, Pd K-edge and the $\text{Au}_{25}\text{Pd}_{0.5}$ sample, Au L_{3} -edge) and fluorescence (the $\text{Au}_{25}\text{Pd}_{0.5}$

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