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Supported bimetallic AuPd clusters using activated Au_{25} clusters

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ABSTRACT

Bimetallic AuPd nanoparticles on alumina supports were prepared using $Au_{25}(SR)_{18}$ precursors activated by mild calcination or $LiBH_4$ treatment, followed by selective deposition of Pd via ascorbic acid reduction. Comparison of their catalytic activity for the oxidation of crotyl alcohol showed that bimetallic structure had significantly improved catalysis compared to Pd/Al_2O_3. In particular, AuPd samples grown from $LiBH_4$-activated Au_{25} clusters exhibit the highest catalytic activity as well as high selectivity towards crotonaldehyde formation, likely due to their smaller particle sizes as compared to AuPd samples grown from calcined Au_{25} clusters. X-ray absorption spectroscopy (XAS) at the Au L_3-edge, Pd L_3-edge and Pd K-edges showed that the resulting bimetallic AuPd nanoparticles had Au-Pd core-shell structures with a 4d-electron poor Pd surface.

1. Introduction

Bimetallic nanoparticles (NPs) are promising catalysts due to their unique catalytic, electronic and optical properties in comparison to the monometallic NPs [1]. Adding a second metal allows for the possibility of tailoring the electronic and geometric structures to enhance the activity and selectivity of NP catalysts, due to changes in electron density and geometries of two different atoms leading to synergistic effects [2,3]. Due to their superior catalytic activities and selectivities, bimetallic NPs are used in numerous reactions, including alcohol oxidations [4], oxidation of other organic compounds [5,6], and catalytic reforming [7]. Particularly, AuPd catalysts have been renowned for their enhanced reactivity and selectivity in several reactions such as the selective oxidation of alcohols and alkenes [8] and CO oxidation [9]. For catalytic reactions, AuPd NPs are typically deposited on oxide supports such as Al_2O_3 [10], SiO_2 [11] and CeO_2 [12] to create highly active heterogeneous catalysts [13]. As a part of the AuPd structure, Au NPs hold great potential for homogeneous and heterogeneous catalysis in various oxidation [14] and hydrogenation reactions [15]. Current interest has been focused on Au clusters, such as Au_{25} [16], Au_{38} [17] or Au_{144} [18] because they have been shown to have unique catalytic behavior when their diameter is smaller than 2 nm [19]. The structure of $Au_{25}(SR)_{18}$ clusters is well characterized by theoretical calculations [20,21] and single-crystal X-ray crystallography [22,23], which show that it exhibits unique geometrical and electronic structures [24]. Because of the extremely small size of $Au_{25}(SR)_{18}$ clusters, they show non-metallic behavior in the form of HOMO-LUMO transitions, and have no surface plasmon resonance band in the UV–vis spectrum. The non-metallic behavior of Au nanoclusters originates from the electron energy quantization effect as a result of ultra-small size, which alters their catalytic properties [25,26].

While Au has interesting catalytic activity on its own, many groups, including our own, have previously shown that AuPd bimetallic NPs are extremely efficient catalysts for low temperature oxidation reactions, including the direct formation of hydrogen peroxide from hydrogen and the room temperature oxidation of allylic alcohols [8,10,27–29]. Our group and others have also shown that the most active species for catalytic activity is typically Au-Pd core-shell particles, in which the Au core withdraws 4d electron density from the Pd shell, thus stabilizing the Pd towards further oxidation [30,31]. Bimetallic $Au_{24}Pd$ clusters have been fabricated by several groups; however, yields of specific AuPd clusters can be very low [32,33]. Nevertheless, they have been shown to be promising model catalysts. For example, Xie and coworkers prepared single Pd atom doped Au_{25} ($PdAu_{24}$) clusters and deposited them on multi-walled carbon nanotubes (CNT) substrate, and found that they had over three times the catalytic activity of Au_{25}/CNT materials for the oxidation of benzyl alcohol [34].

As an alternative strategy to make model AuPd catalysts using Au_{25} clusters, we grew Pd shells onto pre-activated Au_{25} clusters to form well-defined Au-Pd core-shell particles. Here, we prepared AuPd bimetallic NPs using $Au_{25}(SC_2H_4Ph)_{18}$ precursors to form Au

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cores, followed by the deposition of Pd shells. The bimetallic NPs were prepared by a sequential reduction method, using two different methods to activate the Au cores (i.e. in order to remove the thiolate stabilizers), followed by deposition of Pd onto the activated Au cores. The first method involves using mild heat treatment at 250 °C for 2 h to remove the thiolate ligands, while the second involves using a moderate reducing agent, lithium borohydride ($LiBH_4$) to reduce thiolate ligands off the $Au_{25}(SR)_{18}$ clusters. Our previous studies indicated that Au_{25} clusters grew slightly to ca. 2 nm upon calcination at 250 °C [35], while higher calcination temperatures of 500 °C showed significant nanoparticle sintering. EXAFS and XANES analyses were also conducted to elucidate the geometric and electronic structure of our bimetallic NPs. TEM analysis shows that the resulting particle size of bimetallic NPs are 2–3 nm or 4–5 nm depending upon the activation method for Au_{25} precursor, with calcination of Au_{25} clusters leading to larger AuPd NP sizes. EXAFS results indicate that the bimetallic AuPd NPs have core-shell structures and XANES data shows the presence of 4d-electron deficient Pd on the surface of the AuPd NPs. AuPd NPs showed higher catalytic oxidation activities and selectivity toward crotonaldehyde than pure Pd systems.

2. Experimental

2.1. Materials

All chemicals are commercially available and used as received. Tetraoctylammonium bromide (TOAB, 98%), lithium borohydride ($LiBH_4$, 2.0 M in THF), hydrogen tetrachloroaurate (III) trihydrate ($HAuCl_4{\cdot}3H_2O$, 99.9% on metal basis) and porous aluminum oxide (Al_2O_3, 58 Å, ~150 mesh) were purchased from Sigma-Aldrich. Phenylethanethiol (C_8H_9SH, 99%) was purchased from Acros Organics. Palladium (II) acetate was purchased from Alfa Aesar. High purity tetrahydrofuran (THF) was purchased from EMD (HPLC grade). High purity acetonitrile and 100% ethanol were purchased from Sigma-Aldrich. The water used in all experiments was produced with a Milli-Q NANO pure water system (resistivity 18.2 MΩ cm).

2.2. Synthesis of $Au_{25}(SC_2H_4Ph)_{18}$ clusters

The synthesis of $Au_{25}(SC_2H_4Ph)_{18}$ clusters was carried as described previously [36], 50 mL of THF and 500 mg of $HAuCl_4.3H_2O$ were mixed with 1.2 equiv. of TOAB and the solution was slowly stirred for 10 min. Then 5 equivalents of phenylethanethiol was added drop-wise and the solution was stirred until it became transparent. 10 equivalents of $NaBH_4$ in 2 mL ice cold water was added all at once and the final solution was left stirring for 4 days in air. After the reaction was over, the solvent was evaporated using a rotary evaporator and the reaction residue were sequentially washed with copious amounts of 75/25, 85/15 and 90/10 mixtures of ethanol/H_2O. After washing, $Au_{25}(SC_2H_4Ph)_{18}$ clusters were extracted with acetonitrile and the solution was filtered. The filtrate was evaporated using a rotary evaporator and the final clusters dissolved in THF. The yield of the synthesis was 24%.

2.3. Reduction of $Au_{25}(SC_2H_4Ph)_{18}/Al_2O_3$

In order to synthesize clusters supported on alumina, the $Au_{25}(SC_2H_4Ph)_{18}$ clusters were deposited on the Al_2O_3 substrate via a wetness impregnation method, to give a final Au loading of ca. 4 wt%. Two different methods were used to remove the stabilizer; the first involved heating at 250 °C for 2 h under flowing air. The second involved adding 0.02 mL of $LiBH_4$ (2.0 M in THF) to $Au_{25}(SC_2H_4Ph)_{18}/Al_2O_3$ in hexane, and then stirring vigorously for 20 min. The resulting dispersed powder was washed several times with methanol to remove excess reducing agent. After washing, the wet powder was dried in air.

2.4. Preparation of AuPd nanoparticles

Activated Au_{25}/Al_2O_3 materials from above were used for the preparation of sequentially reduced AuPd NPs in various mole ratios; 3:1, 1:1 and 1:3. For the 1:1 AuPd sample, 4.1×10^{-5} moles Au (12.0 mg $Au_{25}(SC_2H_4Ph)_{18}$ clusters before reduction) was deposited on 200 mg of Al_2O_3 substrate. After the activation (thermal or $LiBH_4$ treatment), 8.2×10^{-5} moles (14 mg) of ascorbic acid was added followed by 4.1×10^{-5} moles of Pd(II) acetate (9.1 mg Pd acetate). The 3:1 AuPd and 1:3 AuPd samples were prepared in the same way with different molar ratios.

2.5. Catalytic measurements

The oxidation of crotyl alcohol was conducted at 40 °C for 4 h. The crotyl alcohol was added along with 50 equivalents of catalyst in 3 mL H_2O. The mixture was purged under O_2 during the reaction. A Pd-on-alumina substrate was used as a reference material. To extract the products, 1 mL of $CDCl_3$ was added into the resulting mixture and the mixture was vigorously shaken to transfer the products into the organic phase. The yield, selectivity and conversion were analyzed by ^1H NMR. All the catalytic reactions were repeated 2 times and the results show a good reproducibility. Turnover numbers (TON) were calculated by dividing the moles of product formed by the moles of Pd in the catalyst.

2.6. Characterization

Absorption spectra were recorded on a Varian Cary 50 Bio UV–vis spectrometer with an optical path length of 1 cm and a scan range of 200–1100 nm. Transmission electron microscopy (TEM) analyses of the NPs were conducted using a HT7700 TEM (Hitachi) operating at 200 kV. The Au_{25} and Pd NPs on alumina substrates were thoroughly ground with a small amount of ethanol in a mortar. TEM samples were prepared by drop-casting NPs onto a graphene-coated lacey carbon TEM grid (Electron Microscopy Sciences). Pd K-edge and Au L_3-edge X-ray absorption spectroscopy were conducted on the HXMA (Hard X-ray Micro-Analysis) beamline at Canadian Light Source (CLS) in transmission mode. Pd L_3-edge XANES (X-ray Absorption Near Edge Structure) spectroscopy was also performed at the CLS on the SXRMB (Soft X-ray Microcharacterization Beamline). Pd L_3-edge data was collected in fluorescence mode under a helium atmosphere to reduce beam loss from scattering. The software package IFEFFIT was used for data processing. The EXAFS fitting at the Pd K-edge was performed in the R-space between 1.4–3.0 Å, and bulk Pd fcc bulk lattice parameters were used as a model for fitting. The amplitude reduction factor, $S_o{}^2$, was found to be 0.93 for Pd foil, and that value was used for fitting the bimetallic samples.

3. Result and discussion

Fig. 1 shows the UV–vis spectrum of the as-synthesized $Au_{25}(SC_2H_4Ph)_{18}$ clusters. The spectral features confirm that the Au_{25} sample is nearly monodisperse. The lowest energy band at 685 nm corresponds to the HOMO−LUMO transition due to the Au_{13} core in the Au_{25} structure, and the other two featured bands (associated with the exterior Au_{12} shell in Au_{25} structure) at 445 and 400 nm are assigned to mixed intra-band (sp ⟵ sp) and inter-band (sp ⟵ d) transitions, and an inter-band transition (sp ⟵ d), respectively [23]. We have previously shown that the clusters are nearly monodisperse with sizes of ca. 1 nm by TEM analysis and MALDI mass spectrometry [36].

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