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Publisher's version / Version de l'éditeur:

<https://doi.org/10.1021/jp4063687>

The Journal of Physical Chemistry C, 117, 39, pp. 20007-20016, 2013-09-06

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Following the Thermal Activation of $\text{Au}_{25}(\text{SR})_{18}$ Clusters for Catalysis by X-ray Absorption SpectroscopyAtal Shivhare,[†] Daniel M. Chevrier,[‡] Randy W. Purves,^{†,§} and Robert W. J. Scott^{*,†}[†]Department of Chemistry, University of Saskatchewan, 110 Science Place, Saskatoon, SK S7N 5C9, Canada[‡]Department of Chemistry, Dalhousie University, Halifax, NS, Canada[§]National Research Council of Canada, 110 Gymnasium Place, Saskatoon, SK S7N 0W9, Canada

ABSTRACT: We show the thermal activation of phenylethanethiolate ($\text{L} = \text{SC}_8\text{H}_9$) and hexanethiolate ($\text{L} = \text{SC}_6\text{H}_{13}$) $\text{Au}_{25}\text{L}_{18}$ monolayer protected clusters (MPCs) on carbon black supports, followed by characterization with extended X-ray absorption fine structure (EXAFS) spectroscopy and transmission electron microscopy (TEM). EXAFS analysis shows that the thiolate stabilizers can be partially removed from the surface under mild heating conditions without significant changes in the cluster size. The resulting clusters are shown to be catalytically active for the reduction catalysis of 4-nitrophenol. EXAFS and TEM data show that thermal treatment under air at 200 °C leads to nearly complete removal of all of the thiolate stabilizers with little to no growth in cluster size, while cluster sintering was seen at higher calcination temperatures. The maximum catalytic activity for $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}$ MPCs was seen at 250 °C activation conditions. These results are consistent with results reported earlier for $\text{Au}_{25}(\text{SR})_{18}$ clusters on ceria by Jin et al., who suggested that cluster integrity was maintained during mild activation conditions. Here, EXAFS data unambiguously show that while the cluster size does not grow significantly, such mild heating conditions do lead to nearly complete removal of the thiolate stabilizers.

■ INTRODUCTION

Achievements in the solution phase synthesis and structural characterization of stable and monodisperse Au monolayer-protected clusters (Au_{25} , Au_{38} , Au_{55} , Au_{102} , and Au_{144} MPCs) have been vital for understanding the physical and chemical properties of Au in the nanometer size regime.^{1–5} These clusters have been isolated in good yields and have been shown to act as catalysts for a large number of oxidation, reduction, hydrogenation, and electron transfer catalytic reactions.^{6–12} Recent single crystal structure studies of thiolate protected Au_{25} and Au_{102} clusters have shown that these clusters have a core-shell type structure, with a highly symmetrical core made up of Au atoms and a shell composed of a small variety of Au–thiolate staple motifs containing alternating Au and S atoms.^{13–15} In subsequent studies other clusters were also found to have the similar atomic arrangements.^{16,17} Theoretical studies attribute the stability of these clusters to superatom electronic theory, where the total number of electrons in these clusters is the number required to form a closed electronic shell, and this eventually results in stable architecture.¹⁸ Several experimental studies suggest that thiolate protected Au_{25} clusters do not lose their structural integrity under exposure to mild oxidative and reductive conditions.^{6,11} Other studies have shown that Au_{25} and Au_{55} clusters can survive oxidative etching conditions and remain intact while other clusters decompose under similar conditions.^{19,20} There have been reports in the literature on the thermal activation of $\text{Au}_{25}(\text{SR})_{18}$ MPCs for benzyl alcohol, carbon monoxide oxidation, and

other catalytic reactions.^{9,21,22} These interesting findings clearly suggest that there is an exciting opportunity to further explore the use of $\text{Au}_{25}(\text{SR})_{18}$ MPCs (and other MPCs) as precursors for the development of near-monodisperse supported-Au nanoparticle catalysts. However, as thiols are thought to passivate the surface of supported-Au catalysts due to the strong bonding between Au and S, more needs to be known about the exact mechanisms upon which thiolates can be removed from MPCs with little or no growth in the underlying core size. Herein, we present an EXAFS study on the thermal activation of $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}$ and $\text{Au}_{25}(\text{SC}_6\text{H}_{13})_{18}$ MPCs on mesoporous carbon and show that thiolate removal begins at temperatures as low as 125 °C, and nearly complete thiolate removal can be achieved at temperatures beyond 200 °C. Remarkably, EXAFS and TEM results show that cluster growth due to sintering is negligible under such mild calcination conditions.

Immobilization of nanoparticle catalysts on support materials is important in order to prevent them from sintering, which often leads to a decrease in the catalytic activity. In addition, it is often easier to separate supported catalysts from the reaction mixture after the reaction is over. For example, Jin and co-workers synthesized oxide supported $\text{Au}_{25}\text{L}_{18}$ MPC catalysts for the chemoselective hydrogenation of α,β unsaturated aldehydes

Received: June 27, 2013

Revised: September 5, 2013

Published: September 6, 2013

Figure 1. UV-vis and mass spectra of (a, c) phenylethanethiolate and (b, d) hexanethiolate $\text{Au}_{25}(\text{SR})_{18}$ MPCs.

and ketones to unsaturated alcohols.⁶ Complete selectivity (100%) was observed with both oxide supported and unsupported catalysts, but higher conversion was obtained in the case of the oxide supported catalyst.⁶ Recently it was shown that different oxide supported phenylethanethiolate $\text{Au}_{25}\text{L}_{18}$ MPCs can be used as a catalyst for carbon monoxide oxidation catalysis where the highest catalytic activity was found in the case of cerium oxide supported catalysts activated at 150 °C in an oxygen atmosphere. Experimental data suggested that thiolate stabilizers remained on the surface of Au_{25} clusters and oxidation took place on intact clusters.²¹ Tsukuda and co-workers showed that hydroxyapatite supported $\text{Au}_{25}\text{L}_{18}$ clusters activated at 300 °C can be used for the selective oxidation of styrene to styrene epoxide with 100% conversion and 92% selectivity using *tert*-butyl hydroperoxide as an oxidant.⁸ In related work, Gaur et al. studied the effect of the thermal treatment on titania supported dodecanethiolate $\text{Au}_{38}\text{SR}_{24}$ MPCs and found via EXAFS, TEM, X-ray photoelectron spectroscopy (XPS), and infrared spectroscopy (IR) techniques that thermal treatment at 400 °C led to the complete removal of thiolate stabilizers, and subsequently, the catalyst became active for carbon monoxide oxidation catalysis.¹² While complete thiolate removal was observed at 400 °C, the effect of low temperature heating on the integrity and catalytic behavior of the Au_{38} clusters was not presented.

There have been few studies where an attempt has been made to address the stability of the Au–thiolate bond. Jin and co-workers showed by NMR spectroscopy and mass spectrometry (MS) that two different sulfur-binding modes in glutathione protected Au_{25} MPCs have different oxidative and

thermal stability. Especially above a certain temperature, binding mode-1 which is made up of 12-SR ligands that directly attach to 12 atoms gold core was more stable than the binding mode-2 in which 6-SR ligands are only attached to 12 atoms gold shell. MS revealed $[\text{Au}_{25}\text{SR}_{12}]^-$ intermediates as a prominent species during thermal treatment.²³ Data suggested that this $[\text{Au}_{25}\text{SR}_{12}]^-$ intermediate would form by the loss of 6 thiol molecules which were the part of binding mode-2. Cliffl et al. showed with the help of MS that in the case of tiopronin-protected MPCs, cyclic Au–thiolate tetramers ($\text{Au}_4(\text{SR})_4$) were seen; this may likely be a decomposition product from similar Au MPC staples (although it was not identified as such in the paper).²⁴ Other studies have also shown the loss of $\text{Au}_4(\text{SR})_4$ units during mass spectrometric analysis.^{11,25} These studies suggest that it would be possible to activate $\text{Au}_{25}\text{L}_{18}$ MPCs for catalysis by removing surface staple motifs and Au cluster growth can be controlled by immobilizing them on support materials before activation.

Herein we show a detailed investigation on the thermal activation of several $\text{Au}_{25}(\text{SR})_{18}$ MPCs at various temperatures on mesoporous carbon supports. EXAFS results show that catalytic activation begins at 125 °C under air by partially removing thiolate stabilizers from the surface. EXAFS and TEM results show that mild Au cluster sintering is seen at temperatures between 125 and 200 °C, while above 200 °C rapid Au cluster sintering is seen. We studied nitrophenol reduction catalysis as a model reaction to show that $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}$ MPCs supported on mesoporous carbon can be activated for catalysis under mild heating conditions. Catalytic results for the reduction of nitrophenol with sodium

Figure 2. Au L₃-edge EXAFS fitting in *R*-space of as-synthesized (noncalcined) (a) phenylethanethiolate and (b) hexanethiolate Au₂₅(SR)₁₈ MPCs on carbon.

borohydride show that the catalytic rate constant increases after 125 °C calcination and plateaus at ~200 °C, followed by a decrease in activity for sintered catalysts calcined at 350 °C.

RESULTS AND DISCUSSION

Au₂₅(SC₈H₉)₁₈ and Au₂₅(SC₆H₁₃)₁₈ MPCs were synthesized according to literature procedures.¹¹ The detailed synthetic procedures are described in the Experimental Section. These Au₂₅(SR)₁₈ MPCs were characterized by UV–vis spectroscopy and MS techniques (Figure 1). UV–vis spectra show three major peaks which have been assigned to negatively charged Au₂₅ clusters.²⁶ Mass spectra show molecular ion peaks along with the fragmented peaks and confirm the fact that these clusters are monodisperse MPCs. The second largest fragment peak has been assigned as Au₂₁(SR)₁₄, which forms with the loss of Au₄SR₄ unit. According to the literature Au₄SR₄ units exist as a cyclic tetramer but the mechanism behind its formation is unclear.²³

EXAFS Analysis of Mesoporous Carbon-Supported Phenylethanethiolate and Hexanethiolate Au₂₅(SR)₁₈ MPCs. A detailed procedure for the synthesis of carbon-supported Au₂₅(SC₈H₉)₁₈ and Au₂₅(SC₆H₁₃)₁₈ MPCs is described in the Experimental Section. An inspection of the Au₂₅(SC₈H₉)₁₈ crystal structure reveals that Au₂₅ cluster is composed of an Au₁₃ icosahedron core where the central Au atom is surrounded by 12 gold atoms.¹⁴ This icosahedron core is surrounded by six –S–Au–S–Au–S– staple motifs, where sulfur atoms of the staple motifs are directly attached to the 12 gold atoms of the icosahedron core.¹⁴ EXAFS analysis of these supported clusters was done on the Hard X-ray Microanalysis (HXMA) beamline of Canadian Light Source (CLS) via measurements at the Au L₃-edge. We used a multishell fitting approach to fit Au–S and different Au–Au contributions using phenylethanethiolate Au₂₅L₁₈ MPCs as a model compound following previously published protocols.²⁷ In this multishell fitting approach all Au–Au coordination numbers were fixed (using values from calculated coordination numbers)²⁷ along with the amplitude reduction factor (determined from a Au foil standard), which was fixed at 0.89. Figure 2 shows the experimental Fourier transformed EXAFS (FT-EXAFS) and simulated EXAFS fit for as-synthesized Au₂₅(SC₈H₉)₁₈ and Au₂₅(SC₆H₁₃)₁₈ MPCs. The peaks at ca. 1.9 Å show the Au–S contribution, and the following three peaks at approximately 2.4, 2.8, and 3.2 Å show Au–Au contributions in different bonding environments (nonphase corrected).²⁷ EXAFS fitting parameters for Au₂₅(SC₈H₉)₁₈ and Au₂₅(SC₆H₁₃)₁₈ MPCs are shown in Tables 1 and 2, respectively. The Au–S bond lengths obtained after a two-shell fit were 2.32 and 2.315 Å for

Table 1. EXAFS Fitting Parameters of As-Synthesized Phenylethanethiolate Au₂₅(SR)₁₈ MPCs on Carbon

	CN	<i>R</i> /Å	σ ² /Å ²	<i>E</i> ₀ shift/eV
Au–S	2.0	2.32	0.0053	−0.2
Au–Au(core)	1.44	2.76(2)	0.0079(5)	3(3)
Au–Au(surf)	1.92	3.01(2)	0.0154(2)	3(3)
Au–Au(staple)	2.88	3.3(1)	0.025(5)	3(3)

Table 2. EXAFS Fitting Parameters of As-Synthesized Hexanethiolate Au₂₅(SR)₁₈ MPCs on Carbon

	CN	<i>R</i> /Å	σ ² /Å ²	<i>E</i> ₀ shift/eV
Au–S	1.8	2.315	0.0044	−0.47
Au–Au(core)	1.44	2.805(4)	0.0072(2)	5.3(7)
Au–Au(surf)	1.92	3.02(1)	0.0129(5)	5.3(7)
Au–Au(staple)	2.88	3.32(2)	0.023(1)	5.3(7)

Au₂₅(SC₈H₉)₁₈ and Au₂₅(SC₆H₁₃)₁₈ MPCs, respectively. These match very well with literature values of 2.28–2.39 Å.¹⁴ After fitting the Au–S shell separately using two-shell fit, the Au–S parameters were fixed during multishell Au–Au fitting.²⁷ Au–Au bond lengths of 2.76 Å (Au₂₅(SC₈H₉)₁₈ MPCs) and 2.80 Å (Au₂₅(SC₆H₁₃)₁₈ MPCs) arise from the bonding between the central Au atom of the icosahedron core and surrounding 12 surface gold atoms and also the bond lengths between six short Au–Au pairs which exist in the 12 surface gold atoms of icosahedron. Au–Au bond lengths of 3.01 Å (phenylethanethiolate Au₂₅L₁₈ MPCs) and 3.02 Å (hexanethiolate Au₂₅L₁₈ MPCs) represent the second set of Au–Au pairs present between the 12 surface gold atoms of the icosahedron core with slightly higher bond lengths than the first pair. The third Au–Au bond lengths of 3.3 Å (phenylethanethiolate Au₂₅L₁₈ MPCs) and 3.32 Å (hexanethiolate Au₂₅L₁₈ MPCs) represent the distance between the surface gold atoms and the staple gold atoms. These values are in very good agreement with the literature values reported for Au₂₅(SC₈H₉)₁₈ MPCs.²⁷ Our multishell EXAFS analysis suggests that Au₂₅(SC₈H₉)₁₈ and Au₂₅(SC₆H₁₃)₁₈ MPCs were successfully transferred from solution to solid carbon supports, and they retained their structural integrity before calcination.

Thermal Treatment of Carbon-Supported Phenylethanethiolate and Hexanethiolate Protected Au₂₅(SR)₁₈ MPCs. Au₂₅(SC₈H₉)₁₈ and Au₂₅(SC₆H₁₃)₁₈ MPCs supported on carbon black were thermally treated at different temperatures to study their thermal stability and activation for catalysis. Figure 3 shows the Au L₃-edge FT-EXAFS data at calcination temperatures ranging from 125 to 250 °C. Beyond 125 °C thermal treatments, isolation of different Au–Au

Figure 3. Au L_3 -edge EXAFS data in R -space of the carbon-supported phenylethanethiolate and hexanethiolate Au_{25} clusters thermally treated at different temperatures: (a) $Au_{25}(SC_8H_9)_{18}$ and (b) $Au_{25}(SC_6H_{13})_{18}$ MPCs.

Figure 4. EXAFS fitting of carbon-supported $Au_{25}(SC_8H_9)_{18}$ MPCs calcined at (a) 125, (b) 150, (c) 200, and (d) 250 °C.

Table 3. EXAFS Fitting Parameters of Carbon-Supported Phenylethanethiolate $Au_{25}(SR)_{18}$ MPCs Thermally Treated at Different Temperatures

$T/^\circ\text{C}$	CN (Au–S)	$R/\text{\AA}$ (Au–S)	$\sigma^2/\text{\AA}^2$ (Au–S)	E_0 shift/eV (Au–S)	CN (Au–Au)	$R/\text{\AA}$ (Au–Au)	$\sigma^2/\text{\AA}^2$ Au–Au	E_0 shift/eV (Au–Au)
125	1.11(9)	2.325(4)	0.0034(4)	2(1)	6.3(5)	2.848(4)	0.0089(5)	−1.8(7)
150	0.75(9)	2.331(5)	0.0029(7)	0(1)	7.3(8)	2.852(3)	0.0089(5)	−1.8(7)
200	0.63(8)	2.342(8)	0.0043(7)	1(1)	9.3(3)	2.855(2)	0.0088(2)	−0.4(3)
250	0.5(1)	2.33(2)	0.005(2)	3(3)	10.1(5)	2.855(2)	0.0086(3)	−0.5(4)

Table 4. EXAFS Fitting Parameters of Carbon Black Supported Hexanethiolate $Au_{25}L_{18}$ MPCs Thermally Treated at Different Temperatures

$T/^\circ\text{C}$	CN (Au–S)	$R/\text{\AA}$ (Au–S)	$\sigma^2/\text{\AA}^2$ (Au–S)	E_0 shift/eV (Au–S)	CN (Au–Au)	$R/\text{\AA}$ (Au–Au)	$\sigma^2/\text{\AA}^2$ (Au–Au)	E_0 shift/eV (Au–Au)
125	1.58(6)	2.315(2)	0.0042(3)	0.2(4)	3.6(3)	2.855(3)	0.0091(5)	0.2(4)
150	1.0(1)	2.329(6)	0.0046(8)	2(1)	6.7(4)	2.857(5)	0.0084(3)	0(1)
200	0.8(2)	2.32(2)	0.007(2)	1(4)	9.0(7)	2.851(5)	0.0085(5)	−1(1)

bonding environments was not possible via the multishell fitting approach described in the previous section. This is likely due to the fact that Au–thiolate staples start to be removed from the surface and the structural integrity of the $Au_{25}(SR)_{18}$

MPCs was no longer preserved. Thus, only two-shell fits were conducted using 1 Au–Au and 1 Au–S shell using fcc Au and Au_{25} as structural models.²⁸ Simulated EXAFS fits for $Au_{25}(SC_8H_9)_{18}$ MPCs are shown at each temperature in Figure

4 with corresponding fit parameters for $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}$ and $\text{Au}(\text{SC}_6\text{H}_{13})_{18}$ in Tables 3 and 4, respectively.

For carbon-supported $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}$ MPCs, the Au–Au contribution was still very low after heating at 125 °C, with a CN of 6.3(5), while the Au–S contribution dropped to 1.11(9) from a value of 2.0 for the pristine $\text{Au}_{25}\text{L}_{18}$ cluster. No significant changes in the EXAFS were seen at calcination temperatures below 125 °C; thus, this seems to be the transition temperature where thiolate removal from the gold starts to take place. At a similar calcination temperature, the hexanethiolate MPCs had a significantly lower Au–Au CN of 3.6(3) and a Au–S CN of 1.58(6), which seems to suggest a slightly more thermally stable Au–S bond for this ligand. This data suggests that the Au–S bonds are very vulnerable to decomposition even at low temperature heating, and calcination temperatures of 300 °C or beyond are not necessary for catalytic activation of these clusters.¹² A further increase in temperature to 150 °C brought further changes in Au–Au and Au–S contributions, and it was found that the Au–S contribution dropped significantly in both cases to 0.75(9) and 1.0(1) for $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}$ and $\text{Au}_{25}(\text{SC}_6\text{H}_{13})_{18}$ MPCs, respectively, while the Au–Au contribution further increased to 7.3(8) and 6.7(4), respectively. The increase in Au–Au contribution suggests that the partial removal of thiolate stabilizer from the Au core took place followed by partial sintering. Further increases in temperature resulted in further increases in the Au–Au contributions and decreases in the Au–S contributions, as the removal of thiolate leads to particle sintering. In addition, a small increase in the Au–S bond lengths upon increasing calcination temperature is seen in both cases, although this increase is not large and may not be significant. In addition, the Debye–Waller parameter (σ^2) increases with higher calcination temperatures for the Au–S bond in both systems, indicating a larger degree of disorder for the samples calcined at higher temperatures. There is little to no increase in the Au–Au bond distance. These results suggest that the structure of $\text{Au}_{25}(\text{SR})_{18}$ cluster is very vulnerable to mild heating and thiolate stabilizers can be partially removed with minimal sintering at low temperature.

A TGA analysis of the $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}$ MPCs on carbon in air is shown in Figure 5. The TGA results show that no significant

Figure 5. TGA analysis of carbon-supported $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}$ MPCs in air.

mass loss is seen from the sample until temperatures of ~150 °C, with a major mass loss due to the phenylethanethiol ligands from 150 to 350 °C, followed by a second mass loss at temperatures beyond 350 °C. The first mass loss is in general agreement with the work of Nie et al.,²¹ who showed that although $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}$ MPCs on ceria were activated for CO oxidation at temperatures below 150 °C, no significant mass loss was seen at these temperatures. However, EXAFS results above definitively show that although the phenylethanethiol is not being removed from the sample at such temperatures, ligands are being removed from the Au clusters; they do not remain completely intact. At this time we believe the second mass loss beyond 350 °C is due to the Au-nanoparticle-catalyzed oxidation of the carbon support; pure carbon support samples show no significant mass loss in air until temperatures beyond 500 °C.

TEM analyses of the samples were performed to monitor cluster size growth and correlate size with EXAFS CN values, as shown in Figure 6. It should be noted that it is very difficult to

Figure 6. TEM images of carbon-supported $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}$ MPCs: (a) as synthesized and (b) thermally treated at 125, (c) 200, (d) 250, and (e) 350 °C.

image the clusters at low calcination temperatures and that the limit of resolution (TEM resolution ca. 1 nm) may lead to overestimations of particle sizes. Figure 6a shows the TEM image of $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}$ MPCs supported on carbon black with the cluster size of 1.3 ± 0.1 nm. After calcining these MPCs at 125 °C (Figure 6b) the size increased to 1.5 ± 0.2 nm, and was 1.9 ± 1.1 nm at 250 °C and eventually 2.1 ± 0.9 nm at 350 °C calcination temperatures. TEM results suggest that fairly constant growth in cluster size occurs when the temperature is increased, which is accompanied by the removal of thiols, as previously revealed from our EXAFS analysis. TEM cluster size

analysis suggests that the standard deviations of particle sizes are small at intermediate calcination temperatures, thus suggesting a partial removal of thiols followed by growth as opposed to a more heterogeneous system in which some clusters decompose/sinter while others remain intact. However, we do note that given the resolution limits of TEM, no definitive statements can be made about the absence of unsintered clusters in any of the samples.

Figure 7 shows the correlation between the number of atoms in the clusters and the average first shell coordination number

Figure 7. Number of atoms in a given cluster as a function of first shell coordination number for different geometries. Data were obtained from refs 29–31.

for different geometries determined using studies reported earlier.^{29–31} Analysis of the number of atoms in the clusters using these equations is limited to clusters with closed shells. For clusters with incomplete shells, exact determination of the number of atoms as a function of the coordination number may not be possible, but a general idea about the number of atoms can be obtained by interpolation. It can be seen from Figure 7 that there is a constant growth in number of atoms as a function of first shell coordination number. By comparing these

values with the CNs obtained from EXAFS fitting results (Tables 3 and 4), we can say that there is a constant growth in number of atoms and would result in constant growth in the size as revealed by TEM analysis. After 125 °C calcination of $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}$ and $\text{Au}_{25}(\text{SC}_6\text{H}_{13})_{18}$ MPCs, coordination values obtained from EXAFS analysis were 6.3(5) and 3.6(3), respectively. After correlating these CN values with the number of atoms in the clusters (Figure 7), this suggests that the $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}$ clusters consist of 15–30 Au atoms after calcination at 125 °C and the $\text{Au}_{25}(\text{SC}_6\text{H}_{13})_{18}$ clusters have even fewer Au atoms. These low values (particularly that for $\text{Au}_{25}(\text{SC}_6\text{H}_{13})_{18}$) suggest that there may be some Au sample heterogeneity at such intermediate calcination temperatures; further studies are needed to explain if there is any formation of low coordinated Au sites (i.e., from staples which have been removed from the clusters) which leads to low CN values. After heating at 150 °C, increases in the Au–Au CN for $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}$ MPCs and a significant jump in the Au–Au CN value for $\text{Au}_{25}(\text{SC}_6\text{H}_{13})_{18}$ MPCs were observed. These values suggest further growth in the cluster size as revealed by TEM analysis. Based on the Au–Au CN values obtained at this temperature, the number of atoms in a particle with these CN values could vary from 40 to 80 (Figure 7) depending on the shape it adopts. After heating to 200 and 250 °C, clusters further grew and eventually started to reflect bulk Au nanoparticles with 500 or more atoms in the particles. These results agree well with TEM results in Figure 6 and suggest that the sintering of these MPCs starts to take place beyond ~200 °C due to the fact that surface stabilizers were nearly completely removed from the surface. The combination of EXAFS and TEM data suggests that it is possible to partially remove thiolate stabilizers from the surface of Au_{25} with minimal sintering.

4-Nitrophenol Reduction Catalysis. In 1989, Haruta et al. showed that Au in the nanometer size regime (less than 5 nm) can be used for room temperature carbon monoxide oxidation catalysis.³² Since then there have been many studies focusing on controlling the size of Au nanoparticles in order to study their size dependent catalytic activity for different oxidation and reduction catalytic reactions.^{33–35} Different stabilizers have been used to control the size of gold in nanometer size regime.^{36–39} Of all the stabilizers used, alkanethiols have been commonly used due to very strong

Figure 8. (a) Representative UV–vis spectra showing the progress of the reduction on 4-nitrophenol by a carbon-supported $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}$ catalyst and (b) pseudo-first-order rate fitting of the reduction of 4-nitrophenol by carbon-supported $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}$ MPC catalysts thermally treated at different temperatures.

bonding between gold and sulfur.^{38,1–5} However, this strong bonding is also believed to passivate the surface of Au and hence leaves little surface area available for the catalysis to take place.^{40,41} This problem can be addressed to some extent by either decreasing the size of the Au MPCs or by using less bulky thiol stabilizers.^{6,11} In our previous study we showed that the catalytic activity of thiolate protected Au MPCs for the reduction catalysis of 4-nitrophenol was dependent on the chain length of the thiolate and found that $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}$ MPCs had the highest catalytic activity while $\text{Au}_{25}(\text{SC}_{12}\text{H}_{25})_{18}$ MPCs showed the lowest activity.¹¹ These results suggested that the access of nitrophenolate to the Au surface was a crucial step, and this was somewhat hindered in the case of larger stabilizers. To further increase the accessibility of nitrophenolate to the surface of Au, we examined the carbon-supported calcined samples described above. We used phenylethanethiolate as a protecting ligand because it gave us the highest catalytic activity in the previous study.¹¹ The catalyst was prepared by supporting 0.3% by metal weight $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}$ MPCs on the carbon support (higher loadings of 3% were used for EXAFS analysis in order to obtain good EXAFS data). A detailed procedure for the preparation of the supported catalyst and the catalytic reaction is described in the Experimental Section. Figure 8a shows the UV–vis spectra showing the progress of the catalytic reaction. The peak at 400 nm corresponds to the nitrophenolate peak. This peak decreases with time due to the reduction of nitrophenolate, and a new peak appears at ~ 320 nm due to the formation of aminophenol. This data were fit using the pseudo-first-order rate constant equation where time of the reaction was plotted against $\ln A_0/A$, as shown in Figure 8b.

Figure 9 shows the value of pseudo-first-order rate constant as a function of calcination temperature of the catalyst. The as-

Figure 9. Rate constant for the reduction of 4-nitrophenol using carbon-supported $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}$ MPC catalysts thermally treated at different temperatures.

synthesized (uncalcined) particles on carbon do show some activity (rate constant ca. 0.1 min^{-1}), which is in agreement with previous work.¹¹ We note that the catalytic amounts in this work are ca. 10 times lower than that used for quasi-homogeneous reactions in early work; thus, the rate constant is somewhat lower. Data show that after 125°C calcination the rate constant showed little to no change. A further increase in calcination temperature led to increases in catalytic rate constant, with maximum rate constants of ca. 0.5 min^{-1} seen for calcination at 250°C . Such rates are consistent with literature for unstabilized solid Au nanoparticles in which rates

ranging from 0.1 to 1.0 min^{-1} have been reported.^{42–46} Much lower rates were seen at the higher calcination temperature of 350°C , likely due to particle sintering occurring at this temperature. These results suggest that complete thiolate removal is not necessary for catalytic activity in this system. Data suggest that there are two factors that affect the catalytic activity: the first is the removal of the thiol, and the other is the growth of the clusters via sintering. Our previous study showed that as we increased the steric bulk around the Au_{25} clusters by increasing the chain length of the stabilizers, the catalytic rate constant decreased. It suggests that steric factors are an important factor to be taken into consideration when attempting to modify the catalytic activity. On the basis of this evidence, we can speculate that the enhancement in the catalytic activity would be mainly due to the removal of the thiolate stabilizers. This was further supported by a decrease in rate constant due to sintering when the catalyst was calcined at 350°C .

CONCLUSION

In summary, we have shown that $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}$ and $\text{Au}_{25}(\text{SC}_6\text{H}_{13})_{18}$ MPCs can be supported on carbon supports and activated for catalysis without significantly affecting the structural integrity of the MPCs. These MPCs were thermally activated for 4-nitrophenol reduction catalysis by removing thiolate stabilizers from the surface. EXAFS analysis shows that the thiolate removal from the surface starts to take place at 125°C which was evident by the decrease in Au–S contribution, increase in Au–Au contribution, and nearly complete thiol removal at 250°C where the highest catalytic activity was observed. Further heating at 350°C led to a decrease in the rate constant due to Au cluster sintering. Data also indicated that thiolate removal was accompanied by minimal growth in the cluster size as supported by TEM and EXAFS studies. It also suggests that the access of the nitrophenolate species to the surface of the Au cluster is extremely important for the catalysis to take place, and that this can be achieved by partially removing thiols at intermediate calcination temperatures. In the future, we will focus on studying the activation of these MPCs on oxide supports for oxidation and reduction catalysis, and correlating the activation conditions to the catalytic activity.

EXPERIMENTAL SECTION

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), phenylethanethiol ($\text{C}_8\text{H}_9\text{SH}$, 99%, Acros Organics), 1-hexanethiol ($\text{C}_6\text{H}_{13}\text{SH}$, 97%, Alfa Aesar), sodium borohydride (NaBH_4 , 98%, EMD), and 4-nitrophenol ($\text{C}_6\text{H}_5\text{NO}_3$, 99%, Alfa Aesar) were used as received. Vulcan XC-72R carbon was purchased from Fuel Cell Store. High purity THF (tetrahydrofuran) and acetonitrile were purchased from Fischer Scientific, and 100% ethanol was purchased from Commercial Alcohols. 18 M Ω cm Milli-Q (Millipore, Bedford, MA) deionized water was used throughout.

Synthesis of Phenylethanethiolate and Hexanethiolate $\text{Au}_{25}(\text{SR})_{18}$ MPCs. $\text{Au}_{25}(\text{SR})_{18}$ MPCs were synthesized according to the procedure reported previously.¹¹ Briefly, to the solution of 500 mg of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ in 50 mL of THF, 1.2 equiv of TOAB was added. The resulting solution was stirred for 10 min followed by the addition of 5 equiv of phenylethanethiol or hexanethiol dropwise. This mixture was

stirred until the solution became transparent, and then 10 equiv of NaBH_4 in 5 mL of ice cold water was added all at once. The resulting mixture was stirred in air 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. $\text{Au}_{25}(\text{SC}_6\text{H}_{13})_{18}$ MPCs were extracted with THF, while $\text{Au}_{25}(\text{C}_8\text{H}_9)_{18}$ MPCs were extracted with acetonitrile.

Synthesis of Carbon-Supported $\text{Au}_{25}(\text{SR})_{18}$ MPCs. For EXAFS, TGA, and TEM analysis, carbon supported $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}$ and $\text{Au}_{25}(\text{SC}_6\text{H}_{13})_{18}$ MPCs were prepared by supporting 3% by metal weight of $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}$ and $\text{Au}_{25}(\text{SC}_6\text{H}_{13})_{18}$ MPCs on Vulcan XC-72R carbon. For 4-nitrophenol reduction catalysis the metal loading was maintained at 0.3% by metal weight. A detailed procedure is as follows: first, 100 mg of Vulcan XC-72R carbon was suspended in 25 mL of THF, and the resulting suspension was sonicated for 10 min. To the above suspension, the required amount of $\text{Au}_{25}(\text{SR})_{18}$ MPCs in THF was added dropwise, and the resulting mixture was left for stirring under air for 2 h. After 2 h, the solvent was evaporated first by using a rotary evaporator and finally using a Schlenk line vacuum to ensure complete removal of THF.

Thermal Treatment of Carbon-Supported Au_{25} Clusters. Vulcan XC-72R carbon-supported $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}$ and $\text{Au}_{25}(\text{SC}_6\text{H}_{13})_{18}$ MPCs were thermally treated at 125, 150, 200, 250, and 350 °C under air for 1.5 h using a Lindberg/Blue M furnace. Heating and cooling rates were maintained at 10 °C/min.

4-Nitrophenol Reduction Catalysis. All reactions were done under a N_2 atmosphere. In a typical catalytic reaction, 7 mg of 4-nitrophenol was dissolved in 25/5 mL mixture of THF/water. To this solution, 7 mg of carbon-supported $\text{Au}_{25}(\text{SR})_{18}$ MPCs was added, and the resulting mixture was purged with N_2 for 15 min while stirring. After purging with N_2 , 30 equiv of NaBH_4 in 3 mL of ice cold water was added, and immediately after the addition of NaBH_4 , UV-vis spectra were recorded. The rate constant of the reaction process was determined by measuring the change in the absorbance of the initially observed peak at 400 nm for 4-nitrophenolate as a function of time. Each reaction was done two times to ensure reproducibility. A control experiment was also carried out with just Vulcan XC-72R carbon, and no catalytic activity was observed.

EXAFS Analysis. EXAFS measurements were conducted at HXMA beamline 061D-1 (energy range 5–30 keV; resolution, $1 \times 10^{-4} \Delta E/E$) at the Canadian Light Source (CLS, 2.9 GeV storage ring, 250 mA current). All samples were pressed into pellets and measured in transmission mode at room temperature. A double-crystal Si(111) monochromator was employed for energy selection Au L_3 -edge (11919 eV). Higher harmonics were eliminated by detuning double-crystal Si(111) by using a Rh-coated 100 nm long KB mirror. The incident and transmission X-ray intensities were detected by ion chambers filled with helium–nitrogen mixtures that were installed in front of and behind of the sample cell. The WinXAS 3.2 software package was used to fit the data. Uncertainties in EXAFS fitting results were computed from off-diagonal elements of the correlation matrix, which were weighted by the square root of the reduced chi-squared value obtained for each simulated fit.⁴⁷ The amount of experimental noise was also taken into consideration for each FT-EXAFS spectrum.⁴⁷ For

the data analysis the amplitude reduction factor (S_0^2) was determined from Au foil and fixed at 0.89 for all remaining fits. For data fitting the k -range was chosen from 3.0 to 12.5 $\text{\AA}^{-1}$. A $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}$ MPCs model was used for the analysis of as synthesized carbon black supported $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}$ and $\text{Au}_{25}(\text{SC}_6\text{H}_{13})_{18}$ MPCs,¹⁴ and for thermally activated samples Au–S and Au–Au models were used based on Au_2S and fcc Au unit cell dimensions.²⁸ Theoretical phase and scattering amplitudes used in EXAFS fitting were obtained for the aforementioned models using the FEFF8.2 program code.⁴⁸

TEM/MALDI/UV-Vis/TGA Analyses. Transmission electron micrographs of original $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}$ MPCs and after calcination at 125, 150, 200, and 250 °C were obtained on Philips 410 microscope operating at 100 kV, and TEM images of $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}$ MPCs calcined at 350 °C were obtained on Philips CM-10 microscope operating at 80 kV. Typically ~100 nanoparticles were measured to determine average particles sizes. Mass spectrometry analysis was done on an Applied Biosystems 4800 MALDI-TOF/TOF instrument (Frederic, MD) operating in linear positive ion mode using DCTB (trans-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile) as a matrix. A mixture of ubiquitin and insulin was used as an external standard. Absorption spectra were recorded on a Varian Cary 50 Bio UV-vis spectrometer with an optical path length of 1 cm. Thermal gravimetric analyses (TGA) were performed using a TA Instruments TGA Q5000IR under air flow. Samples were run from 25 to 500 °C with a heating rate of 5 °C/min.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge financial assistance from the National Sciences and Engineering Research Council of Canada (NSERC) and thank Ning Chen at the Canadian Light Source for assistance with XAS measurements. We also acknowledge the very helpful assistance of Mahdi Hesari and Mark Workentin at Western University with $\text{Au}_{25}\text{L}_{18}$ synthesis and purification. EXAFS experiments described in this paper was performed at the Canadian Light Source, which is supported by the Natural Sciences and Engineering Research Council of Canada, the National Research Council Canada, the Canadian Institutes of Health Research, the Province of Saskatchewan, Western Economic Diversification Canada, and the University of Saskatchewan.

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