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COMMUNICATION

Oxidative decomposition of Au₂₅(SR)₁₈ clusters in a catalytic context

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Gold nanoparticle catalysis of chemical transformations has emerged as a subject of intense interest over the past decade. In particular, Au₂₅(SR)₁₈ has emerged as a model catalyst. In an effort to investigate their potential as intact, homogeneous, unsupported catalysts, we have discovered that Au₂₅(SR)₁₈ clusters are not stable in oxidizing conditions reported for catalytic styrene oxidation. Further investigation suggests that the active catalytic species is an Au(I) species resulting from oxidative decomposition of the starting gold cluster. This conclusion appears independent of R-group on thiolate-protected Au₂₅(SR)₁₈ clusters.

Due in part to the noble nature of bulk gold, the advent of gold based catalytic transformations is recent.^{1, 2} The work of Hutchings and Haruta established selective oxidation of hydrocarbons and low-temperature CO oxidation by supported gold clusters and nanoparticles.^{3, 4} A variety of other reactions catalysed by ligated gold nanoclusters are also recently investigated, with both phosphine and thiolate protected clusters proposed as catalytic species.⁵ In supported catalysis, the ligands are often removed by calcination.⁶

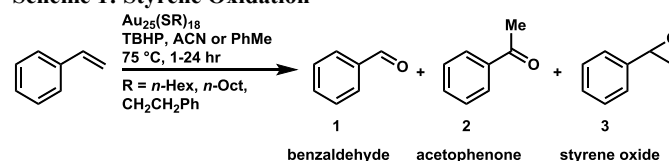
Of all ligated clusters, the Au₂₅(SR)₁₈ nanocluster stands out as a widely studied model system for catalysis.⁶ Since its initial discovery,⁷ the Au₂₅(SR)₁₈ cluster has been synthesized with an array of R groups, including saturated alkanes, aromatic species (e.g. 4-mercaptobenzoic acid, 4-bromothiophenol), phenylethane (R = CH₂CH₂Ph), and small polypeptides like glutathione, with syntheses reproduced in many labs.⁸⁻¹⁵ Au₂₅(SR)₁₈ clusters are isolable and stable in 3 different charge states: -1, 0, and +1 with solved crystal structures for the -1 (R = CH₂CH₂Ph)^{14, 16} and 0 (R = CH₂CH₂, CH₂CH₂Ph)^{10, 14, 17} charge states represented in the literature.

Au₂₅(SR)₁₈ clusters calcinated on support are reported for the 1,2-reduction of α,β -unsaturated ketones, reduction of aryl nitro groups, and oxidation of alkenes.^{6, 18, 19} Au₂₅(SR)₁₈ clusters adsorbed on

support without calcination are reported as effective catalysts for styrene oxidation.²⁰ In addition, there are scattered reports of homogeneous catalysis using intact Au₂₅(SR)₁₈ clusters.^{21, 22}

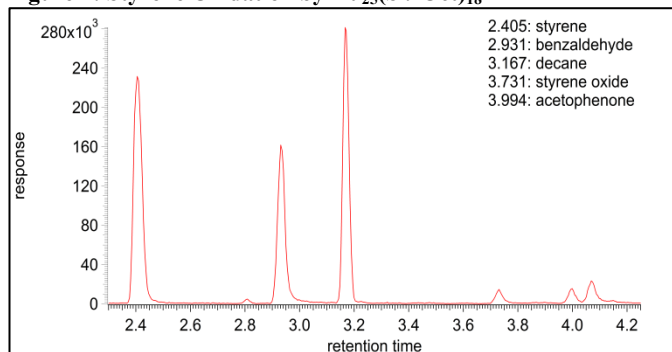
We report here an initial reinvestigation of homogeneous catalysis with Au₂₅(SR)₁₈ clusters, stemming from our long-standing interest in the properties of small gold clusters.²³⁻²⁸ Homogeneous catalysis often offers a distinct benefit with respect to product selectivity, and affords the opportunity to take advantage the unique properties of Au₂₅(SR)₁₈ clusters without the practical and conceptual complexity introduced by support and calcination.

Scheme 1: Styrene Oxidation



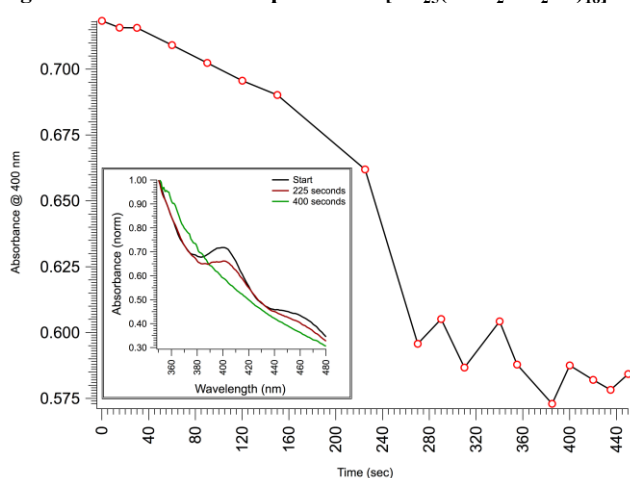
We began our investigation by examining oxidative cleavage of styrene (Scheme 1). This model reaction was selected for several reasons: it has been reported by multiple research groups,^{6,20} the starting materials are inexpensive, and the product mixtures are well-suited for quantitative analysis by gas chromatography.^{6, 20, 29}

We found that while we could reproduce the catalytic products previously reported, Au₂₅(SR)₁₈ clusters are not stable to oxidizing reaction conditions similar to those reported by Jin.¹⁸ Further investigation suggests that the active catalytic species is an Au(I) species that results from oxidative decomposition of Au₂₅(SR)₁₈. This conclusion is supported by comparison of catalytic activity of Au₂₅(SR)₁₈, the Au-thiol polymer precursor, and Au₂₅(SR)₁₈ decomposition products. Kinetic catalyst poisoning experiments also suggest a mononuclear gold species as the active catalyst, and X-ray photoelectron spectroscopy (XPS) data also point toward a mononuclear Au(I) species.

Figure 1: Styrene Oxidation by Au₂₅(Sn-Oct)₁₈

We began our investigation into the catalytic behaviour of homogeneous Au₂₅(SR)₁₈ clusters by replicating results previously reported.^{6,20} Figure 1 shows the GC trace from this initial experiment, with the expected product peaks indicated. After 24 hrs at 75 °C in CHCl₃, we observed product distributions similar to those previously reported, although at lower conversion. During the course of these early experiments, we observed little no difference in conversion between 6 and 24 hours reaction time, and also no differences between reactions run under ambient visible light or in the darkness.

To establish cluster lifetime under the oxidative reaction conditions – typically employing 167 equivalents of *t*-butylhydrogenperoxide (TBHP) to Au₂₅(SR)₁₈ cluster – we exposed the clusters to TBHP (167 equiv to Au₂₅) at 37 °C and monitored the resulting mixture by ultraviolet/visible spectroscopy. Figure 2 shows decomposition of Au₂₅(SR)₁₈ as judged by the disappearance of the characteristic absorbance peaks of the cluster. An absorbance peak at 400 nm is one characteristic of [Au₂₅(SR)₁₈]⁰ spectra; this and all other distinctive features disappear within 5 minutes even at the reduced temperature.³⁰ Decomposition occurs before significant conversion to product is seen, even at elevated temperature (Supplemental Information, S75). This result led us to consider the possibility that the active catalytic species in styrene oxidation was not the cluster itself, but rather oxidative decomposition products of Au₂₅(SR)₁₈. Oxidative decomposition of Au clusters by H₂O₂ and iodine have been reported previously,^{31, 32} and as such decomposition by a similarly strong oxidant, TBHP, is unsurprising.

Figure 2: Oxidative decomposition of [Au₂₅(SCH₂CH₂Ph)₁₈]⁰

To interrogate the active Au species in this catalytic styrene oxidation, independent of their origin, we compared catalysis by initially intact Au₂₅(SR)₁₈, Au₂₅(SR)₁₈ that is oxidatively decomposed prior to use as a catalyst, and the Au(I)-SR oligomers or polymers that are a precursor to Au₂₅(SR)₁₈. To decompose the Au₂₅(SR)₁₈ before the catalytic reaction we added TBHP to a solution of Au₂₅(SR)₁₈, heated for 10 minutes at 75 °C, allowed the reaction to cool to room temperature, added styrene, and reheated to 75 °C.

Table 1: Cluster, polymer, and decomposition products

Entry	Starting gold species	Solvent	%Conversion to PhCHO (std err)
1	[Au ₂₅ (PET) ₁₈] ⁰	PhMe	2.30 (0.14)
2 ^a	Au-(PET) polymer	PhMe	10.5 (3.72)
3 ^b	decomposed [Au ₂₅ (PET) ₁₈] ⁰	PhMe	6.79 (1.18)
4	[Au ₂₅ (PET) ₁₈] ⁰	ACN	0.33 (0.15)
5 ^a	Au-(PET) polymer	ACN	1.51 (0.37)
6 ^b	decomposed [Au ₂₅ (PET) ₁₈] ⁰	ACN	1.34 (0.03)
7 ^a	Au-(Sn-Hex) polymer	PhMe	10.5 (2.55)
8 ^b	decomposed [Au ₂₅ (Sn-Hex) ₁₈] ⁰	PhMe	13.0 (0.96)
9 ^a	Au-(Sn-Hex) polymer	ACN	4.19 (1.28)
10 ^b	decomposed [Au ₂₅ (Sn-Hex) ₁₈] ⁰	ACN	1.28 (0.04)
11	[Au ₂₅ (Sn-Oct) ₁₈] ⁰	PhMe	10.5 (2.07)
12 ^a	Au-(Sn-Oct) polymer	PhMe	9.88 (3.42)
13 ^b	decomposed [Au ₂₅ (Sn-Oct) ₁₈] ⁰	PhMe	9.79 (1.41)
14	[Au ₂₅ (Sn-Oct) ₁₈] ⁻¹	ACN	4.72 (0.79)
15 ^a	Au-(Sn-Oct) polymer	ACN	2.22 (0.51)
16 ^b	decomposed [Au ₂₅ (Sn-Oct) ₁₈] ⁰	ACN	1.27 (0.07)

Reaction conditions: 25 mol % Au in PhMe (0.078 M), 0.157 mmol styrene and 0.275 mmol TBHP at 75 °C for 1 hr. ^aPolymer synthesized as described in supporting information (S4). ^bClusters were decomposed as described in the text, detailed procedure in the supplemental information (S4)

As can be seen in Table 1 (entries 3 and 6), *oxidatively decomposing the Au₂₅(SR)₁₈ cluster before beginning the catalytic reaction results in a more active catalyst*. We observed a three-fold increase in conversion to benzaldehyde at 1 hr with Au₂₅(PET)₁₈.³³ Further studies using *n*-hexanethiol and *n*-octanethiol ligated clusters gave similar results (Table 1, entries 7-16). To further probe if the cluster was necessary for oxidative cleavage of styrene, we tested the Au₂₅(SR)₁₈ precursors in the reaction. Table 1 (entries 2, 5, 7, 9, 12 and 15) shows the results of these experiments. As can be seen, the Au-SR polymeric precursor gave similar results to the oxidatively decomposed Au₂₅(SR)₁₈ cluster. At 1 hr of reaction time we observed benzaldehyde as the sole product under each set of reaction conditions tested above. Table 1, entry 14 used the (-1) rather than (0) charge state of the starting cluster to examine if this had any effect on overall catalytic behaviour. As can be seen, it did not. Taken together these results indicate that intact Au₂₅(SR)₁₈ clusters are not necessary for the oxidative cleavage of alkenes, and that mononuclear Au species are likely the active catalyst.

Further support for this conclusion comes from kinetic poisoning experiments. Kinetic poisoning is commonly used to differentiate between mononuclear metal species and small clusters as the active catalyst.^{34, 35} Experiments of this sort have been quite informative in other catalytic gold reactions,^{36, 37} and we surmised that kinetic poisoning would be equally useful here. In general, if a monometallic species is the active catalyst, it is expected that one or more equivalents of poison will be required to fully inhibit the catalytic reaction. If a polymetallic species is the active catalyst, it is expected that less than one equivalent of poison will be required. The structure of Au₂₅(SR)₁₈ shows 12 Au atoms on the surface with thiolate ligands. Of these, two have significant solvent exposure and four others are solvent exposed to some degree.³⁸ Thus we expect that any Au₂₅(SR)₁₈ cluster should have two highly active sites for

catalysis, although up to six may be possible.^{21, 38} Therefore, if the intact clusters are the active catalytic species less than one equivalent of poison *per gold atom* should substantially decrease the reaction rate. However, if a mononuclear Au species is the active catalyst, at least one equivalent of poison *per gold atom* should be required to substantially attenuate catalysis. This follows methodology established by Finke for differentiation of nanocluster catalysis from homogeneous, mononuclear catalysis in other systems.^{35, 39}

We conducted poisoning experiments using diphenylphosphinoferrrocene (dppf) and triphenylphosphine (PPh₃) as poisons. These compounds were chosen as based on our observation that Au(PPh₃)Cl was not a competent catalyst for styrene oxidation (supplemental information, figures S77 and S78). Additionally, triphenylphosphine has been previously used to poison gold-catalyzed reactions.⁴⁰ We hypothesized that dppf, being bidentate and having a large bite angle, would sequester any Au(I) species without leaving any free coordination sites. Triphenylphosphine was used for comparison in the event that free iron from decomposition of dppf muddied the results of those experiments.

Table 2 shows the results of our kinetic poisoning investigation. As can be seen from entries 1 and 4, addition of small amounts of phosphine gives a result similar to that from the decomposed cluster (Table 1, entry 3). In order to observe meaningful reductions in rate, 10 equivalents of poison per Au atom were required, corresponding to 250 equivalents per intact Au₂₅(SR)₁₈ cluster. We were concerned; however, that consumption of the oxidant by oxidation of the phosphine could be a confounding factor in our results. Further poisoning studies were conducted with 1,3-dimethylbenzimidazolium iodide. Addition of base to this precursor gives an *N*-heterocyclic carbene (NHC), which binds gold with high affinity and cannot be oxidized by the oxidant.⁴¹ As can be seen in Table 2 (entries 7-10), 250 equivalents of poison to cluster were also required to halt catalysis in this case. These results, taken together, are highly indicative of a mononuclear gold species as the active catalyst.

Table 2: Kinetic poisoning results

Entry	Poison	Equiv to Au	Equiv to Au ₂₅ (PET) ₁₈	Conversion to PhCHO (%)
1 ^a	dppf ^b	0.040	1.00	8.35 (1.70)
2 ^a	dppf	2.00	50.0	7.99 (1.93)
3 ^a	dppf	10.0	250.0	3.03 (0.73)
4 ^c	PPh ₃	0.040	1.00	7.37
5 ^c	PPh ₃	2.00	50.0	3.38
6 ^c	PPh ₃	10.0	250.0	0.22
7 ^c	N/A	0.00	0.00	18.8
8 ^c	NHC	0.040	1.00	17.9
9 ^c	NHC	2.00	50.0	3.51
10 ^c	NHC	10.0	250.0	0.00

Entries 1-6 run for 1 hr in PhMe (0.078 M), with 1 mol percent [Au₂₅(PET)₁₈]⁰ and 0.157 mmol styrene at 75 °C. Entries 7-10 run for 75 min in CHCl₃ (0.078 M), with 1 mol percent [Au₂₅(PET)₁₈]¹ and 0.135 mmol styrene at 75 °C. NHC is not soluble in PhMe.

^a Average of 3 trials, with standard error in parentheses.

^b diphenylphosphinoferrrocene

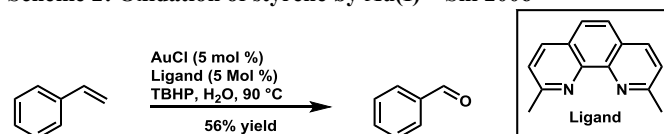
^c Single run, shown for comparison

To further probe the structure of the active catalyst, we undertook XPS of both the Au₂₅(PET)₁₈ precursor polymer and the oxidative decomposition products of Au₂₅(PET)₁₈. The precursor and oxidative decomposition products show the Au 4f_{7/2} peak at 84.8 eV and 85.6 eV, respectively. These are consistent with Au(I) species previously reported in the literature.⁴² ¹H NMR of the decomposition product suffers interference from the Au nucleus and is of low quality.

However, COSY spectra of the decomposition product show no signals off of the diagonal, indicating no through-space interactions. These data, when evaluated as a whole, indicate that Au(I)-thiolate species are likely the active catalyst in this reaction. Spectra are presented in the supplemental information (S64, S80).

In addition to our data, there are similar reports of Au(I) catalysed oxidative cleavage of alkenes using mononuclear Au(I) species. In 2006, Shi and co-workers reported using AuCl and an organic ligand to cleave a number of alkenes, generally with high yields (Scheme 2).⁴³

Scheme 2: Oxidation of styrene by Au(I) – Shi 2006



Although their reaction was optimized using aqueous conditions, they report comparable results using PhMe as the solvent (reference 36, Table 1, entries 4 and 5). These results show that oxidative alkene cleavage with mononuclear gold species and TBHP is possible under a variety of reaction conditions, further implicating mononuclear gold species in those reactions previously reported for Au₂₅(SR)₁₈.

In addition to the above, we have conducted preliminary decomposition experiments with Au₂₅(SR)₁₈ clusters adsorbed on silica gel support without calcination. These experiments are presented in the supplemental information, pages S66 and S67. While not dispositive, early results show that supported clusters decompose when exposed to TBHP and elevated temperature.

Conclusions

Interest in the chemical reactivity of thiolate-protected gold nanoclusters has grown substantially in the last several years,² and our findings raise an important question about the potential for such applications. While our results are silent on calcinated Au₂₅(SR)₁₈ catalysts, it is clear that unsupported Au₂₅(SR)₁₈ clusters are unstable under oxidative reaction conditions previously reported. Furthermore, our results using acetonitrile as solvent indicate that unsupported Au₂₅(SR)₁₈ clusters are not stable to these reaction conditions even when used as a heterogeneous suspension. In light of our findings, recent literature reports may need to be re-evaluated.^{6, 20} Overall, our data support the conclusion that mononuclear Au(I) species are the active catalyst in the oxidative cleavage of styrenes, at least in the case of catalysis with unsupported clusters.

Despite the remarkable stability of Au₂₅(SR)₁₈ nanoclusters, questions remain regarding their viability as homogeneous catalysts.¹⁴ The nature of the true catalytic species is an important consideration in reaction development, especially within the realm of atomically defined nanoclusters.^{34, 44} While these species have immense potential owing to their aforementioned stability and unique electronic properties, that potential can only be fully realized by exploiting reactions wherein the clusters themselves are likely to survive.

Herein we have presented evidence that not only are Au₂₅(SR)₁₈ clusters unstable to oxidations with TBHP, but also that the Au-thiol cluster precursor and cluster decomposition products are

equally effective in the oxidation of styrene. Even at temperatures significantly lower than that of the reaction, TBHP completely decomposes Au₂₅(SR)₁₈ before notable product appearance is observed. Further, kinetic poisoning experiments have shown that far more than one equivalent of phosphine poison per Au₂₅(SR)₁₈ cluster active site is required to observe any meaningful reduction in reaction rate – indicating that the active catalytic species is not likely the intact cluster. Lastly, XPS studies show that the Au species present after decomposition and before cluster formation are Au(I), which indicates that Au(I) thiolates are likely the active catalyst in this reaction.

Notes and references

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Electronic Supplementary Information (ESI) available: Full experimental details, along with chromatographic and spectroscopic data are included in the supplemental information. See DOI: 10.1039/c000000x/

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