Controlled, Autocatalytic Formation of Gold Nanoparticles from (CH$_3$)$_2$Au(acac)

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Introduction

Gold nanoparticles (AuNPs) dispersed on reducible oxide supports show high activities and selectivities in a variety of oxidation reactions, including the low-temperature CO oxidation. The catalytic properties of these materials are a strong function of the AuNP's size and shape, so control over these properties is key catalyst optimization.

Thermal decomposition of the volatile organometallic complex (CH$_3$)$_2$Au(acac) (acac = acetylacetonate) is a well-known methodology for the synthesis of AuNPs both in solution and on heterogeneous supports. In order to better understand this process, a series of thermal decompositions of (CH$_3$)$_2$Au(acac) were conducted in various solvents and on a heterogeneous silica support. These studies were augmented with DFT calculations of various support and solvent models, which provided insight into the mechanism of this transformation.

The conversion of (CH$_3$)$_2$Au(acac) into AuNPs in solution was monitored using UV-Vis spectroscopy. In thoroughly dried solvents, this process is extremely slow; however, addition of protic acids drastically increases the rates of decomposition. In addition, the apparent decomposition mechanism shows a strong solvent dependence.[1]

Silica supported samples of (CH$_3$)$_2$Au(acac) can be prepared by vapor deposition of complex onto a thermally pretreated silica.[2] Thermal treatment of these materials can be monitored using in situ IR spectroscopy, which reveal an unexpectedly complex AuNP formation mechanism. These spectra also captured a novel, decomposition intermediate.

A number of models structures were compared using density functional theory (DFT) calculations. These quantum chemical calculations gave relative energies and predicted spectral properties, which provide valuable insight into the decomposition mechanism. In addition, they were key to characterizing our mysterious support intermediate.
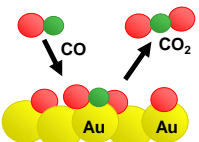
(1) *Organometallics* **1989**, *8*, 2477-2482.
(2) *Appl. Phys. Lett.* **1985**, *47*, 538-540.

DFT Calculations
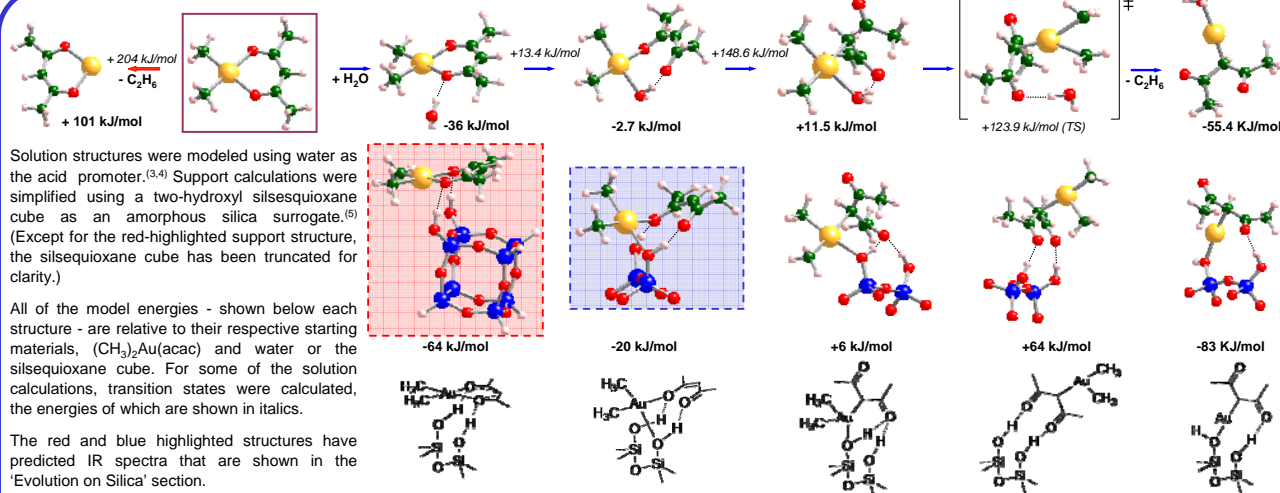
Solution structures were modeled using water as the acid promoter.[3,4] Support calculations were simplified using a two-hydroxyl silsesquioxane cube as an amorphous silica surrogate.[5] (Except for the red-highlighted support structure, the silsesquioxane cube has been truncated for clarity.)

All of the model energies - shown below each structure - are relative to their respective starting materials, (CH$_3$)$_2$Au(acac) and water or the silsesquioxane cube. For some of the solution calculations, transition states were calculated, the energies of which are shown in italics.

The red and blue highlighted structures have predicted IR spectra that are shown in the 'Evolution on Silica' section.

(3) *J. Am. Chem. Soc.* **1977**, *99*, 3695–3704.
(4) *J. Am. Chem. Soc.* **1976**, *98*, 7599-7607.
(5) *J. Phys. Chem. C* **2009**, *113*, 8794–8805.

DFT calculations performed using the quantum chemical package Gaussian 03.
DFT Functional = B3LYP; Basis Sets: Au = Mod. Lanl2DZ, Other atoms = 6-31Gd'

Evolution in Solution

A. Several isosbestic points are observed during the course of the reaction, indicative of a transformation without intermediate buildup. 304 nm (CH$_3$)$_2$Au(acac); 272 nm acetylacetone (Hacac); 540-560 nm surface plasmon resonance of the AuNPs. The change in plasmon absorption maximum is due to increasing particle size.
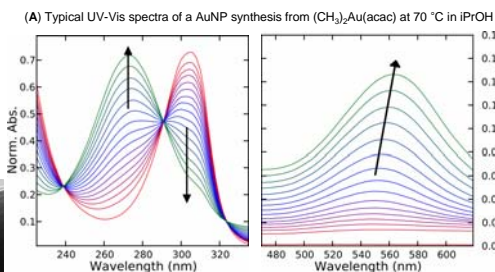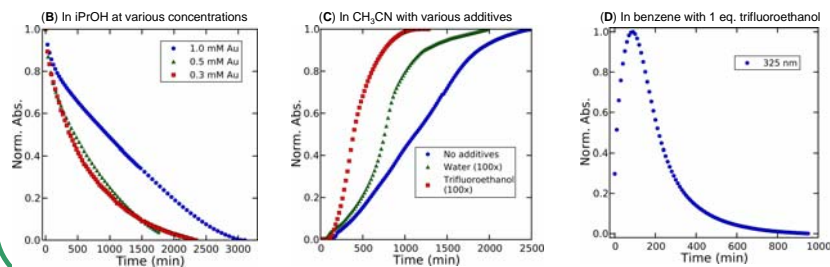
TEM of AuNPs taken in collaboration with Seshadri Group in MRL

(A) Typical UV-Vis spectra of a AuNP synthesis from (CH$_3$)$_2$Au(acac) at 70 °C in iPrOH
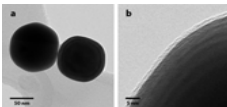
B. An increase in decomposition rate with a decrease in gold concentration in dried iPrOH and measured at 304 nm. In addition, the reaction order appears to change from pseudo-zero to first order.

C. Acids increase the autocatalytic decomposition rate in dried CH$_3$CN as measured at 540 nm; the effect seems to be related to acid strength: water pK_a = 31.4; trifluoroethanol pK_a = 23.5. (pK_a values measured in dimethylsulfoxide)

D. With small additions of acids in dried benzene, an intermediate is clearly formed during the decomposition.
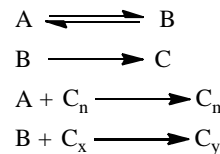

(B) In iPrOH at various concentrations

(C) In CH$_3$CN with various additives

(D) In benzene with 1 eq. trifluoroethanol

Evolution on Silica

IR spectra taken during the thermal decomposition of (CH$_3$)$_2$Au(acac) on silica

(A)
(B)
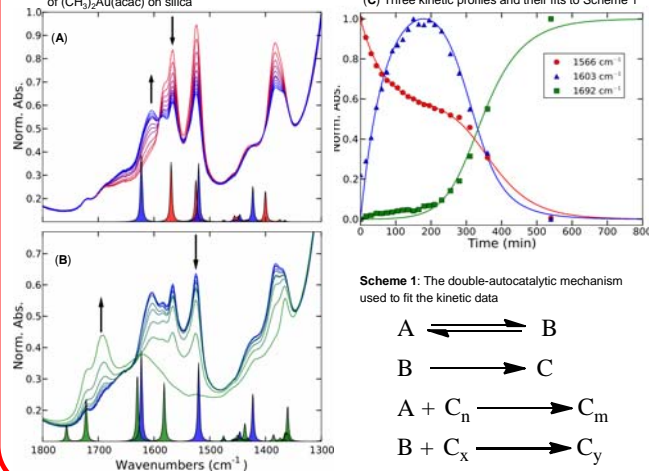
(C) Three kinetic profiles and their fits to Scheme 1
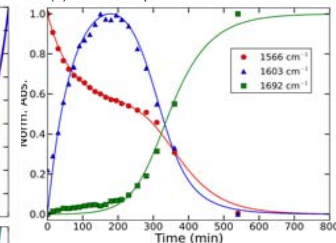
Scheme 1: The double-autocatalytic mechanism used to fit the kinetic data

$$A \rightleftharpoons B$$
$$B \longrightarrow C$$
$$A + C_n \longrightarrow C_m$$
$$B + C_x \longrightarrow C_y$$

A. IR spectra taken during the first 150 minutes of thermal degradation of (CH$_3$)$_2$Au(acac) supported on SiO$_2$ at 70 °C (the lines are the measured data). An isosbestic point at 1600 cm^{-1} suggests a clean transformation without intermediate buildup. The filled curves below the data are the DFT predicted spectra for the red- and blue-highlighted models in the 'DFT Calculations' section. (The predicted frequencies were scaled by 0.97 in order to highlight the overlap with the measured spectra.)

B. IR spectra taken from 150 minutes to ~1200 minutes. Again, a new isosbestic point is observed at 1650 cm^{-1}. The filled blue curve is equivalent to the figure above; the green filled curve is a 1:1 overlap the predicted spectra of the keto and enol tautomers of Hacac hydrogen bound to a silsesquioxane cube (Not shown).

C. Three distinct kinetic profiles were extracted from in situ IR spectra in Figures A and B (shown as the solid points). This unusual kinetic profile was fit to the double-autocatalytic decomposition mechanism shown in Scheme 1 (shown as lines).[6] (One data point was truncated at 1200 min.) This is the minimal kinetic model necessary to fit this data.

(6) *J. Am. Chem. Soc.* **2005**, *127*, 8179-8184.

Conclusions

The transformation of (CH$_3$)$_2$Au(acac) to AuNPs, both in solution and on a silica support, is an extremely complex process. In solution, the rate and apparent mechanism are strongly affected by the nature of the solvent and acid promoter, and on silica supports, another mechanism is observed by in situ IR spectroscopy. However, comparison of the overall kinetic profile seen on silica with those observed in solution shows a mirroring of many features, suggesting related mechanisms. A quantitative fit to the biphasic kinetics observed in the supported experiment is obtained using a double-autocatalytic decomposition mechanism.[6] DFT calculations provide a series of potential decompostion intermediates, the structures and energies of which are similar in both the solution and support models. In addition, the predicted IR spectra match closely with the observed spectra and are key to identifying the novel decomposition intermediate.