

## Genesis of a Highly Active Cerium Oxide-Supported Gold Nanocluster Catalyst for CO Oxidation

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### Introduction

Gold on hydroxylated metal oxide supports has been discovered to be surprisingly active and selective for numerous reactions, the most thoroughly investigated of them being CO oxidation.[1] Recent results determined by X-ray absorption near edge structure (XANES)[1,2] spectroscopy, temperature-programmed oxidation and reduction,[3] Mössbauer spectroscopy,[4] and X-ray photoelectron spectroscopy identify cationic gold in supported gold catalysts and point to its involvement in the catalytic sites for CO oxidation.[2,3,4,5] The properties of these gold catalysts are support-dependent, and high-area (nanostructured and defect-rich) cerium oxide has been found to give highly active CO oxidation catalysts. We prepared a highly active gold catalyst for CO oxidation by combining the advantages of the nanostructured cerium oxide support with the advantages of highly dispersed cationic gold formed from the organometallic precursor Au(CH<sub>3</sub>)<sub>2</sub>(acac) [acac is acetylacetonate, CH<sub>3</sub>COCHCOCH<sub>3</sub>]. We summarize the synthesis and characterization of this catalyst and its performance for CO oxidation.

### Materials and Methods

Samples were synthesized and handled in the absence of moisture and air. The catalyst, containing 1 wt% Au, was synthesized from Au(CH<sub>3</sub>)<sub>2</sub>(acac) (Strem 99.9%) and high-surface-area CeO<sub>2</sub> (Daiichi, 99.9%, 173 m<sup>2</sup>/g; average particle diameter 46 nm). The sample was prepared by forming a slurry of Au(CH<sub>3</sub>)<sub>2</sub>(acac) in *n*-pentane with CeO<sub>2</sub> powder that had been partially dehydroxylated under vacuum at 673 K. The slurry was stirred for 24 h, and the solvent was removed by evacuation for 24 h. The catalyst was tested in a once-through flow reactor for CO oxidation, with on-line product analysis by gas chromatography and mass spectrometry. Reactions were carried out at atmospheric pressure and temperatures in the range of 298–353 K with 15.2 Torr of CO and 7.6 Torr of O<sub>2</sub>. Catalyst samples, both before and after use for CO oxidation, were characterized by EXAFS, XANES, and IR spectroscopies.

### Results and Discussion

EXAFS characterization of the as-prepared sample showed that within EXAFS resolution the gold species were site-isolated and mononuclear, as indicated by the absence of any detectable Au–Au contributions. The XANES signature indicates cationic gold. The catalyst was tested for CO oxidation over a range of temperatures and with various pretreatments. Activity data for the catalyst are summarized in Table 1 (values of turnover frequency (TOF) were determined from differential conversions); a comparison is given with other high-area-oxide-supported catalysts investigated under similar conditions.

Used catalyst samples taken after various times on stream were characterized by EXAFS spectroscopy, with the results after short times indicating the presence of catalysts without detectable Au–Au contributions (mononuclear gold complexes) and the results at later

time indicating an Au–Au first-shell coordination number of approximately 4, indicating the presence of clusters that can be modeled approximately as Au<sub>6</sub>. XANES features of the latter are intermediate between those of the cationic gold complexes and zerovalent gold, consistent with nanoclusters that are too small to be considered metallic. As these clusters formed, the activity of the catalyst increased, indicating a higher activity of the clusters than of the mononuclear complexes.

**Table 1. Comparison of activities of supported gold catalysts for CO oxidation**

Catalyst	Approximate average cluster diameter/ nm	T/K	TOF/s <sup>-1</sup>	Time on stream/h
Au/CeO <sub>2</sub> <sup>*</sup>	<sup>a</sup>	333	2.5 × 10 <sup>-3</sup>	2.5
Au/CeO <sub>2</sub> <sup>*</sup>	4	353	<sup>b</sup>	24
Au/La <sub>2</sub> O <sub>3</sub> <sup>6a</sup>	<sup>a</sup>	298	3.2 × 10 <sup>-2</sup>	50
Au/CeO <sub>2-x</sub> <sup>6b</sup>	4	298	2 × 10 <sup>-2</sup>	10
Au/zeolite NaY <sup>6c</sup>	<sup>a</sup>	298	3 × 10 <sup>-3</sup>	1
Au/Al <sub>2</sub> O <sub>3</sub> <sup>6d</sup>	2.4	273	2 × 10 <sup>-2</sup>	>0.5
Au/Fe <sub>2</sub> O <sub>3</sub> <sup>6e</sup>	<1	293	<sup>b</sup>	10

<sup>\*</sup>This work. <sup>a</sup>Au–Au contributions were undetectable by EXAFS spectroscopy.

<sup>b</sup>Conversion too high to be differential and not sufficient for determination of TOF.

### Significance

The present work demonstrates the activity of a mononuclear supported gold catalyst and its activation as these complexes are converted into nanoclusters approximated as Au<sub>6</sub>. The catalyst is highly active for CO oxidation. This is the first demonstration of activity of gold complexes and gold clusters separately.

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