

# Genesis of Gold Clusters from Mononuclear Gold Complexes on TiO<sub>2</sub>: Reduction and Aggregation of Gold Characterized by Time-Resolved X-Ray Absorption Spectroscopy

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Mononuclear gold complexes bonded to TiO<sub>2</sub> were synthesized from Au(CH<sub>3</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>), and their decomposition and conversion into gold nanoclusters on the TiO<sub>2</sub> surface were characterized by time-resolved X-ray absorption and infrared spectroscopies as the temperature of the sample in flowing helium was ramped up. Mass spectra of the evolved gases were also measured during this process. The results show (a) the onset of formation of CH<sub>4</sub> as a decomposition product, (b) the reduction of Au<sup>III</sup> to Au<sup>0</sup>, and (c) the formation of Au–Au bonds, all occurring in approximately the same temperature range (about 335–353 K), indicating that the reduction and aggregation of the supported gold are simultaneous processes facilitated by the removal of methyl ligands initially bonded to the gold. IR spectra recorded during the treatment indicate that water on the TiO<sub>2</sub> surface may be involved in the process by reacting with methyl groups bonded to Au<sup>III</sup> to give CH<sub>4</sub>.

## Introduction

Although bulk gold is barely reactive, gold highly dispersed on supports such as metal oxides is highly reactive and catalytically active for numerous reactions, including CO oxidation,<sup>2</sup> propene epoxidation,<sup>2</sup> vinyl chloride synthesis,<sup>3</sup> and others.<sup>4</sup> Typical supported gold catalysts are structurally complex and incorporate gold nanoparticles of various sizes and shapes, and many of them also incorporate gold cations.<sup>5,6</sup> It has been shown that cationic gold alone on a zeolite support catalyzes CO oxidation,<sup>7</sup> but catalysts containing both cationic and zerovalent gold are more active than those containing only cationic gold,<sup>8</sup> suggesting that both cationic and zerovalent gold play a role in the catalysis.

The steady-state activities of MgO-supported CO oxidation catalysts containing both cationic and zerovalent gold increased with the fraction of gold that was cationic, as determined by temperature-programmed reduction and temperature-programmed oxidation.<sup>9</sup> In contrast, gold bilayers supported on TiO<sub>2</sub> monolayers mounted on molybdenum oxide single crystals are also reported to be highly active CO oxidation catalysts, and zerovalent or even anionic gold has been implicated, with no evidence of cationic gold.<sup>10</sup> Thus, the individual roles of cationic and zerovalent gold on supports remain to be resolved. The available reports include characterization of the oxidation state(s) of the gold in supported gold catalysts before and after use and during steady-state operation,<sup>9</sup> but there are hardly any reports of the characterization of supported metal catalysts in transient operation by time-resolved techniques.<sup>11</sup>

As a step toward resolution of the roles of cationic and zerovalent gold in supported catalysts, we characterized the conversion of supported cationic gold into reduced, aggregated gold. Supported cationic gold complexes were prepared from the precursor Au<sup>III</sup>(CH<sub>3</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>), as before.<sup>5</sup> This was adsorbed on TiO<sub>2</sub>, because this support gives some of the most active catalysts for CO oxidation.<sup>12</sup> We used several techniques in concert in transient experiments to characterize the progress

of reduction and aggregation of the gold on TiO<sub>2</sub>, showing how these processes are coupled. Specifically, we converted supported cationic gold complexes into gold clusters by autoreduction, following the changes as the sample was being heated in He by time-resolved extended X-ray absorption fine structure (EXAFS), X-ray absorption near edge structure (XANES), and infrared (IR) spectroscopies, combined with mass spectrometry of the evolved gases.

## Experimental Section

Sample syntheses and transfers were done with exclusion of air and moisture. The sample, containing 1 wt % gold, was prepared by bringing Au<sup>III</sup>(CH<sub>3</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>) (Strem, 98%) in contact with TiO<sub>2</sub> (P-25, Degussa, a mixture of anatase and rutile), which had been partially dehydroxylated under vacuum at 673 K, as described elsewhere.<sup>13</sup> Time-resolved X-ray absorption spectra were recorded at beamline MR-CAT of the Advanced Photon Source at the Argonne National Laboratory as the initially prepared sample was treated in He in a flow reactor/cell<sup>14</sup> at temperatures increasing at 3 K/min from 298 to 448 K. The temperature was controlled with a microprocessor-based temperature controller (Omega). The errors in temperature are estimated to be a few K. Every 2 min, an XANES/EXAFS spectrum was recorded as before.<sup>7</sup>

Samples, pressed into self-supporting wafers for characterization by IR spectroscopy, were loaded into a cell (In-situ Research Institute, Inc., South Bend, IN) in a N<sub>2</sub>-filled glovebox. The cell was connected to a vacuum/adsorption system, which allowed recording of spectra while He flowed through and around the wafer at 760 Torr as the temperature was ramped from 298 to 573 K at 3 K/min. Spectra were recorded with a Bruker IFS 66v spectrometer with a spectral resolution of 4 cm<sup>-1</sup>. Each reported spectrum is the average of 128 scans.

The IR cell also served as a flow reactor, and mass spectra of the effluent gases were measured as the IR spectra were recorded. The instrument was an on-line Balzers OmniStar mass spectrometer running in multiion monitoring mode. The changes in the signal intensities of the main fragments of CH<sub>4</sub> (*m/e* =

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**TABLE 1: EXAFS Results Characterizing the Supported Species Formed during Treatment of the Initially Prepared TiO<sub>2</sub>-supported Au<sup>III</sup> Complexes in Flowing He at Increasing Temperature<sup>a</sup>**

shell	<i>N</i>	<i>R</i> (Å)	$10^3 \times \Delta\sigma^2$ (Å <sup>2</sup> )	$\Delta E_0$ (eV)
treatment temperature, 298 K				
Au–Au	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
Au–O	2.1 ± 0.1	2.15 ± 0.01	7.0 ± 0.7	−2.5 ± 0.4
Au–C	1.8 ± 0.2	2.04 ± 0.01	8.4 ± 0.8	15.0 ± 0.6
Au–Ti	0.7 ± 0.2	3.23 ± 0.03	10.0 ± 1.2	−5.1 ± 0.6
treatment temperature, 335 K				
Au–Au	0.3 ± 0.1	2.80 ± 0.01	1.3 ± 0.9	−4.5 ± 0.5
Au–O	1.4 ± 0.1	2.19 ± 0.01	−0.4 ± 0.7	−0.5 ± 0.6
Au–O	0.3 ± 0.2	2.77 ± 0.02	9.4 ± 0.7	1.3 ± 0.4
Au–Ti	1.1 ± 0.2	3.13 ± 0.03	−4.4 ± 1.3	−4.9 ± 0.8
treatment temperature, 390 K				
Au–Au	5.0 ± 0.1	2.78 ± 0.01	9.1 ± 1.2	−1.2 ± 0.5
Au–Au 2 <sup>nd</sup>	2.1 ± 0.2	4.03 ± 0.02	12.1 ± 1.3	5.7 ± 0.7
Au–O	0.4 ± 0.1	2.20 ± 0.01	6.4 ± 1.1	−3.0 ± 0.9

<sup>a</sup> Notation: *N*, coordination number; *R*, distance between absorber and backscatterer atoms;  $\Delta\sigma^2$ , Debye–Waller factor;  $\Delta E_0$ , inner potential correction. <sup>b</sup> Undetectable. The error bounds represent precisions determined with the XDAP software based on repeat measurements; they are not accuracies.

12, 13, 14, 15, 16) and CO<sub>2</sub> (*m/e* = 16, 28, 30, 44) were recorded. Because both CH<sub>4</sub> and CO<sub>2</sub> give signals at *m/e* = 16, the analysis characterizing CH<sub>4</sub> was based on changes in intensity of the signal unique to methane at *m/e* = 15. Signals are reported relative to that of the He carrier gas at *m/e* = 4 to remove effects of small pressure fluctuations.

**Analysis of EXAFS Data.** Analysis of the EXAFS spectra to obtain structural parameters was done by a difference fit technique embedded in the software XDAP,<sup>15</sup> as before.<sup>7</sup>

## Results

**Characterization of Initially Prepared Supported Gold Complexes.** EXAFS spectra characterizing the initially prepared sample in flowing He at 298 K indicate the presence of mononuclear gold complexes bonded to TiO<sub>2</sub>, as evidenced by the lack of detectable Au–Au contributions and the presence of approximately two oxygen atoms at an Au–O distance of approximately 2.15 Å (Table 1), similar to typical metal–oxygen bonding distances found in a number of metal oxide-supported mononuclear group 8 metal complexes.<sup>16</sup>

The EXAFS data also indicate approximately two carbon atoms per Au atom at a distance of 2.04 Å, consistent with retention in the supported complex of the methyl groups of the precursor Au<sup>III</sup>(CH<sub>3</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>). These results are bolstered by the presence of  $\nu_{\text{CH}}$  bands in the IR spectrum, at 2868, 2930, and 2960 cm<sup>−1</sup> (which are also present in the spectrum of crystalline Au<sup>III</sup>(CH<sub>3</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>) (Supporting Information), indicative of methyl groups. IR bands were also observed at 1377, 1442, 1528, and 1600 cm<sup>−1</sup>; these are characteristic of C<sub>5</sub>H<sub>7</sub>O<sub>2</sub> ligands bonded to Ti centers of the support,<sup>17</sup> but not C<sub>5</sub>H<sub>7</sub>O<sub>2</sub> ligands bonded to gold—they are not present in the spectra of crystalline Au<sup>III</sup>(CH<sub>3</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>) (Supporting Information).<sup>18</sup>

In summary, these observations are consistent with the reaction of Au<sup>III</sup>(CH<sub>3</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>) with partially dehydroxylated TiO<sub>2</sub> to give (a) complexes incorporating Au(CH<sub>3</sub>)<sub>2</sub> groups bonded to two oxygen atoms of the TiO<sub>2</sub> surface and (b) surface Ti(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>) groups.

XANES spectra characterizing the initially prepared sample in the presence of flowing He at 298 K bolster the IR results indicating the presence of Au<sup>III</sup>, as evidenced by the following features in the spectra, which are characteristic of Au<sup>III</sup>

complexes, both in the crystalline state and on supports: (a) the position of the absorption edge at 11923 eV, (b) the presence of a prominent feature centered at an energy 4 eV higher than the absorption edge (white line), and (c) the presence of shoulders at 15 and 50 eV higher than the X-ray absorption edge, all of which are typically observed in XANES spectra of complexes containing Au<sup>III</sup>; details of these results have been reported.<sup>5,13</sup>

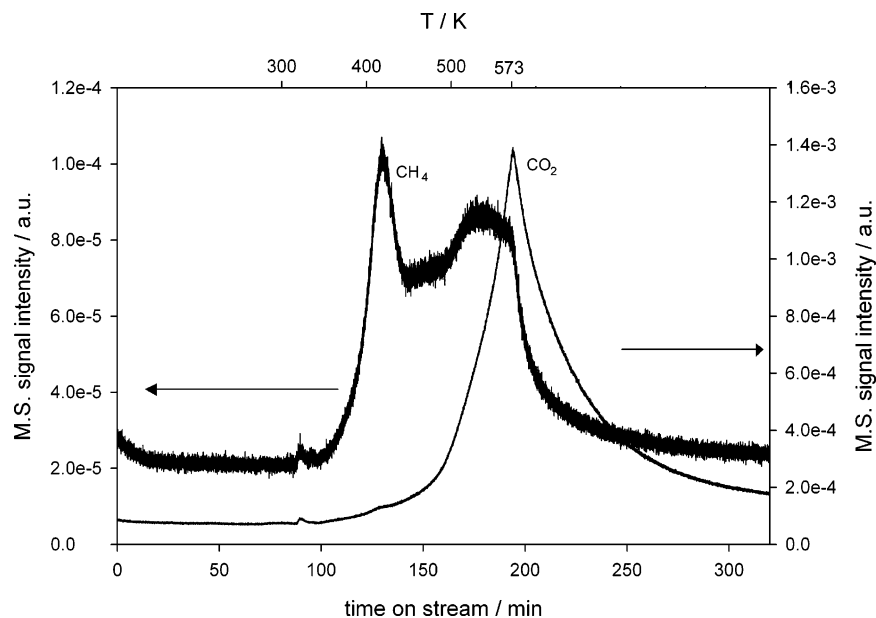
**Characterization of Supported Samples during Reduction and Aggregation of the Gold.** *IR/Mass Spectrometry.* IR spectra of the sample recorded as it was heated in flowing He show a decrease in intensity of the broad band at 3400 cm<sup>−1</sup> indicative of molecular water (Supporting Information).<sup>19</sup> As this band disappeared, a new band appeared at 3660 cm<sup>−1</sup>, indicative of hydrogen-bonded OH groups on the anatase phase of TiO<sub>2</sub>.<sup>19</sup>

Mass spectra representing the gases formed as the initially prepared sample was treated in flowing He at increasing temperatures (Figure 1) give no evidence of the formation of any products at temperatures below 335 K. As the temperature reached approximately this value, however, CH<sub>4</sub> became evident in the gas phase effluent, and its concentration increased rapidly as the temperature was ramped to 410 K, whereupon it reached a local maximum (Figure 1). At a higher temperature, approximately 490 K, another increase in the formation rate of CH<sub>4</sub> became evident (Figure 1), and CO<sub>2</sub> was observed simultaneously. The formation rate of each of these products reached a local maximum at about 573 K, then declining as the temperature was held constant at this value. No gas-phase products were observed after the treatment of the sample at 573 K had continued for 2 h. These results indicate the removal of the organic ligands derived from Au<sup>III</sup>(CH<sub>3</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>).

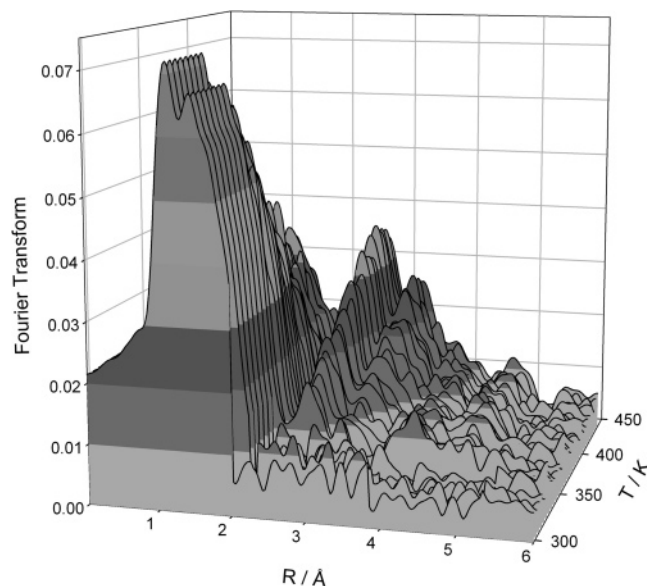
*EXAFS Spectroscopy.* Time-resolved EXAFS spectra recorded as the initially prepared sample was treated in flowing He during the temperature ramp<sup>20</sup> indicate the presence of mononuclear gold complexes at temperatures lower than about 335 K, as evidenced by the lack of detectable Au–Au contributions (Table 1). When the temperature reached 335 K, however, the EXAFS spectrum indicated that a new shell was beginning to appear (Figure 2). This was fitted with a fractional Au–Au coordination number (Table 1, Figure 3A,B). It indicates the onset of aggregation of the gold. The rapid increase in both the Au–Au coordination number and the rate of formation of methane occurred in nearly the same temperature ranges (Figures 1 and 4).

As the temperature increased further to 390 K, the Au–Au coordination number increased from approximately 0.3 to 5 (Table 1, Figure 3C–D and Figure 4), thereafter remaining nearly constant as the temperature increased to 448 K. No further change in the Au–Au coordination number was observed after the sample had been treated in He at 448 K for an additional 2 h.

*XANES Spectroscopy.* The XANES indicate a continuous decrease in intensity of the white line as the temperature was ramped from 298 to about 353 K (Figure 5). No further change in this intensity was observed at higher temperatures. In contrast, the intensities of the XANES peaks characteristic of cationic gold (at 5 and 50 eV beyond the absorption edge) remained nearly constant as the temperature increased from 298 to 353 K; but at 353 K these peaks disappeared within 2 min, being replaced by new peaks at 15 and 25 eV beyond the absorption edge (Figure 5, inset). Simultaneous with these changes, the position of the absorption edge shifted from 11 923 to 11 919 eV. Finally, the XANES spectrum became indistinguishable



**Figure 1.** Changes in intensity of the mass spectral signals of the effluent gases from the flow reactor when the sample made by bringing Au<sup>III</sup>-(CH<sub>3</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>) in contact with partially dehydroxylated TiO<sub>2</sub> was treated in flowing He at increasing temperature.



**Figure 2.** Radial distribution of the time-resolved EXAFS spectra recorded as the sample made by bringing Au<sup>III</sup>-(CH<sub>3</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>) in contact with TiO<sub>2</sub> was treated in flowing He at increasing temperature. The radial positions were not corrected for phase shifts.

from that of gold foil (Supporting Information). No further changes in the spectra were observed as a result of treatment at higher temperatures. These results indicate autoreduction of the initially present Au<sup>III</sup> to Au<sup>0</sup> as the sample was treated in flowing He at increasing temperatures.

**Summary.** The IR, EXAFS, XANES, and mass spectrometric data are consistent in showing changes associated with reduction and aggregation of the supported gold, and the temperature of the onset of the major changes indicated by all these data was in the range of about 335–353 K.

## Discussion

### Formation of Supported Mononuclear Complexes of Au<sup>III</sup>.

The results show that Au<sup>III</sup>-(CH<sub>3</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>) reacts with the partially dehydroxylated surface of TiO<sub>2</sub> to give site-isolated mononuclear complexes of Au(CH<sub>3</sub>)<sub>2</sub> bonded to two oxygen

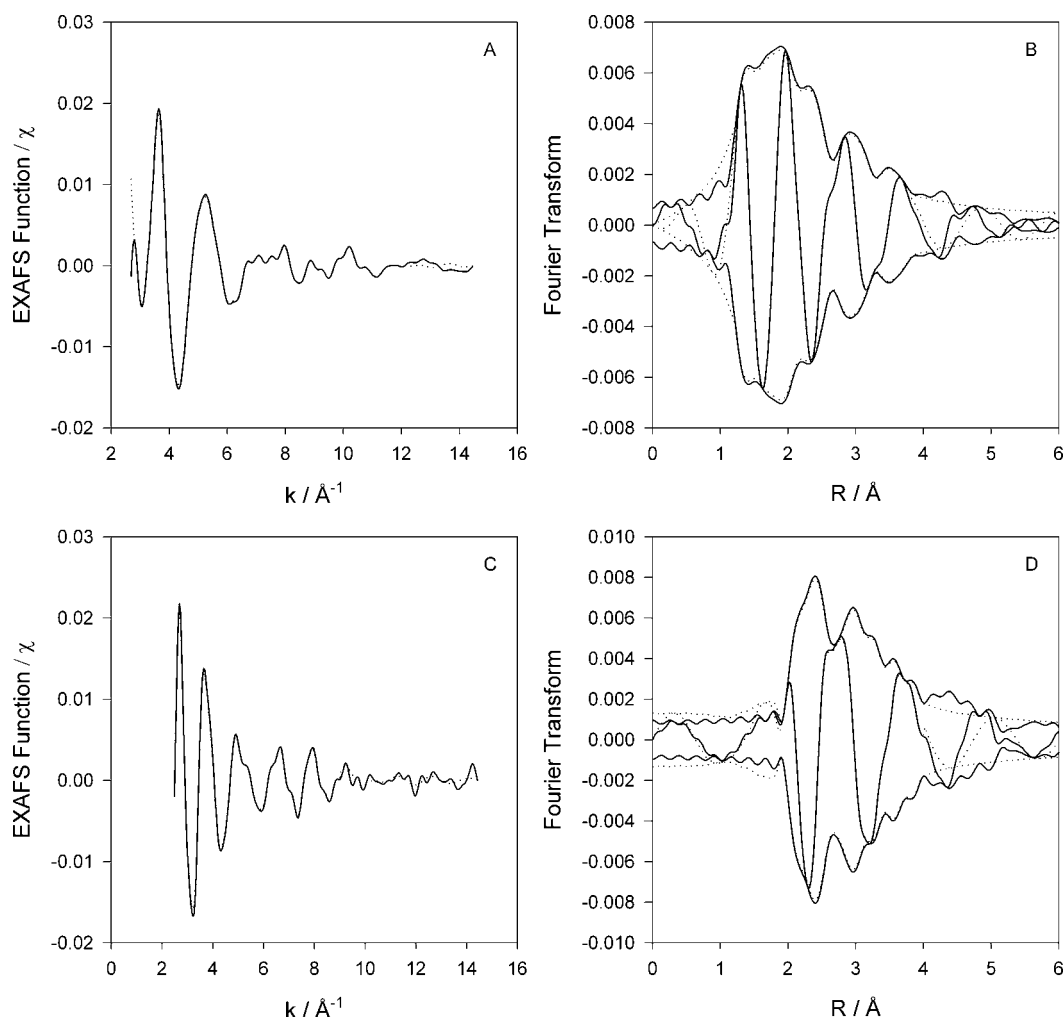
atoms of the support. Analogous reactions have been observed to occur between Au<sup>III</sup>-(CH<sub>3</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>) and other metal oxides<sup>18,22</sup> to give similar supported mononuclear gold complexes. In all these samples, XANES spectra indicate the presence of Au<sup>III</sup>, demonstrating that the reaction of the precursor with the surface of the support does not lead to reduction of the gold.

**Simultaneous Reduction and Aggregation of Supported Gold.** The results showing the decomposition of Au(CH<sub>3</sub>)<sub>2</sub> bonded to the surface of TiO<sub>2</sub> in flowing He as the temperature increased indicate the formation of CH<sub>4</sub> starting at about 335 K. Because the IR spectra show decreasing intensities of both the band characterizing molecular water on TiO<sub>2</sub> and those characteristic of methyl groups, with a concomitant increase in intensity of the band at 3660 cm<sup>-1</sup> that characterizes hydrogen-bonded hydroxyl groups on the anatase phase of TiO<sub>2</sub> (Supporting Information), we suggest that the decomposition of the gold complex resulted from the reaction of methyl groups bonded to gold with molecular water on the support to give CH<sub>4</sub> and surface hydroxyl groups. However, because of the possible interconversion of surface water and hydroxyl groups, we cannot rule out the possibility that the decomposition may involve methyl groups and surface hydroxyl groups.

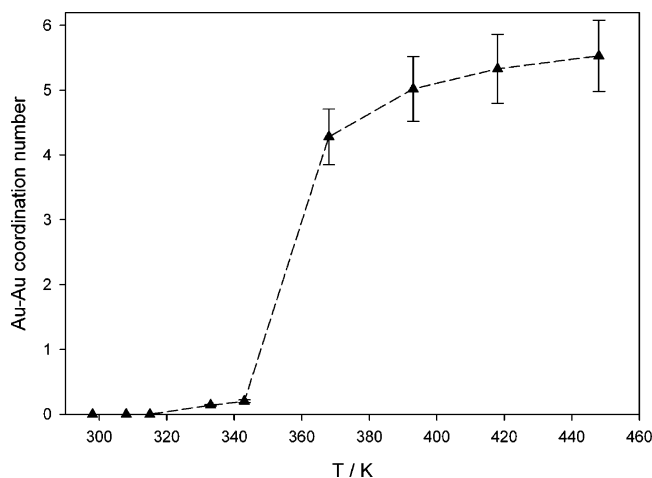
As methyl groups reacted and left the surface, forming CH<sub>4</sub>, Au–Au bonds formed simultaneously, as evidenced by the appearance of the Au–Au contribution in the EXAFS spectra at about 335 K. The Au–Au distance is characteristic of Au–Au bonds in supported gold clusters,<sup>5</sup> and their appearance thus indicates the migration and aggregation of the gold on the TiO<sub>2</sub>.

The XANES spectra, specifically, the features characteristic of zerovalent gold, indicate major changes in the gold starting to take place at a temperature not much higher than the 335 K at which the onset of methane formation and the first formation of Au–Au bonds were observed. The temperature of onset of changes in the XANES is imprecise, in part because the XANES features are not sharp (Figure 5, inset).

We emphasize that the XANES features reflect more than just changes in the oxidation state of the gold. The XANES is also influenced by the nature of the ligands coordinated to the gold, the symmetry of the complexes, and the size of any supported gold clusters.<sup>23</sup> Some unresolved combination of these explains the continuous change in the white line intensity (Figure



**Figure 3.** Results of EXAFS analysis characterizing the  $\text{TiO}_2$ -supported gold sample formed by adsorption of  $\text{Au}^{\text{III}}(\text{CH}_3)_2(\text{C}_5\text{H}_7\text{O}_2)$  on  $\text{TiO}_2$ : (A) Experimental EXAFS function (solid line) and sum of the calculated contributions (dotted line) for the sample treated in flowing He at 335 K. (B) Imaginary part and magnitude of uncorrected Fourier Transform ( $k^0$ -weighted) of experimental EXAFS function (solid line) and sum of the calculated contributions (dotted line) for the sample treated in flowing He at 335 K. (C) Experimental EXAFS function (solid line) and sum of the calculated contributions (dotted line) for the sample treated in flowing He at 390 K. (D) Imaginary part and magnitude of uncorrected Fourier transform ( $k^0$ -weighted) of experimental EXAFS function (solid line) and sum of the calculated contributions (dotted line) for the sample treated in flowing He at 390 K.



**Figure 4.** Temperature dependence of the Au–Au coordination number estimated from time-resolved EXAFS spectra recorded as the sample made by bringing  $\text{Au}^{\text{III}}(\text{CH}_3)_2(\text{C}_5\text{H}_7\text{O}_2)$  in contact with partially dehydroxylated  $\text{TiO}_2$  was treated in flowing He at increasing temperature.

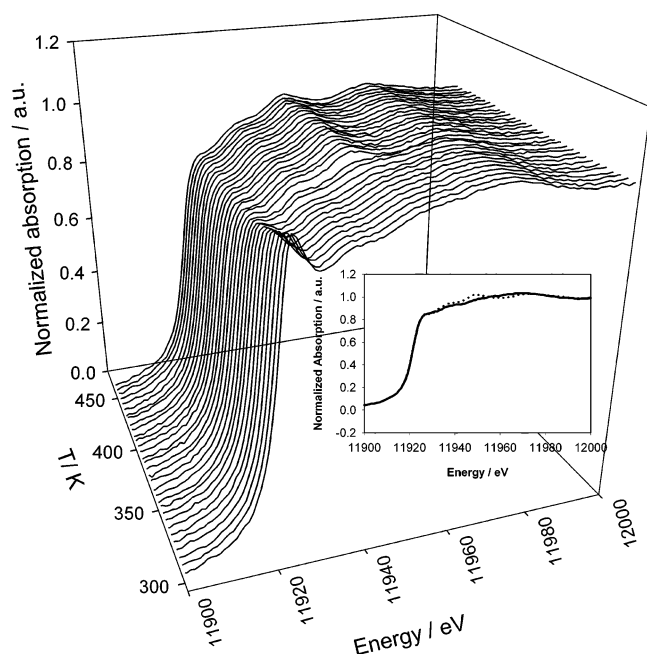
5), even at temperatures lower than that at which aggregation of the gold was evident (Figure 2); evidently changes preceding

migration and aggregation of the gold were taking place at these lower temperatures.

As the treatment temperature increased, the uniformity of the surface species decreased, as evidenced by the appearance of Au–Au contributions at 335 K (when the aggregation of the gold evidently started). The fractional Au–Au coordination number (Table 1) suggests the presence of mixtures of gold species, presumably including mononuclear (cationic) gold complexes and (zerovalent) gold clusters of various sizes and shapes on the support. The presence of mixtures complicates the assignment of oxidation state(s) of the gold on the basis of XANES spectra. XANES provides at best only qualitative information about the oxidation state(s) of supported gold when mixtures are present.

The degree of reduction and aggregation of the gold is clearly correlated with the degree of removal of the methyl groups (Figures 1, 2, and 5). The gold in the initially prepared sample was present in the form of tetracoordinated 16-electron species ( $\text{Au}(\text{CH}_3)_2$  bonded to two oxygen atoms of the  $\text{TiO}_2$  support). As the sample was heated and reaction occurred, with the release of  $\text{CH}_4$ , coordinatively unsaturated gold complexes must have formed, and these are expected to be highly reactive. In other words, as methyl ligands coordinated to the gold reacted with





**Figure 5.** XANES spectra characterizing the sample made by bringing Au<sup>III</sup>(CH<sub>3</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>) in contact with partially dehydroxylated TiO<sub>2</sub> as it was treated in flowing He at increasing temperature. Inset: Consecutive XANES spectra recorded at approximately 353 K (solid) and at 355 K (dotted).

groups (inferred to be water or hydroxyl groups on the support) to give CH<sub>4</sub>. Au atoms are inferred to have satisfied their tendency to become coordinatively saturated by migrating on the support and, in the absence of reactive molecules in the gas phase, coordinating to other gold atoms to form nanoclusters.

**Implications for Catalysis.** Inasmuch as the reactants in CO oxidation catalysis are both reducing and oxidizing agents, and reduction of cationic gold is accompanied by formation of nanoclusters of zerovalent gold, it is expected that the balance between cationic gold and gold nanoclusters—and thus the catalytic activity—can be tuned by the reaction conditions, including the ratio of CO to O<sub>2</sub> in the reaction mixture. The facile conversion of cationic to zerovalent gold emphasizes the importance of investigating supported gold catalysts in the functioning state if a goal is to resolve the roles of cationic and zerovalent gold.

## Conclusions

Mononuclear Au<sup>III</sup> complexes bonded to the surface of TiO<sub>2</sub> were formed by the reaction of Au<sup>III</sup>(CH<sub>3</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>) with partially dehydroxylated TiO<sub>2</sub>. By means of time-resolved spectroscopy, we were able to follow the decomposition of these surface complexes as the temperature was ramped up. IR and mass spectra recorded during the treatment show that the formation of CH<sub>4</sub> coincides with the removal of methyl groups from the gold, inferred to result from reaction with water or hydroxyl groups on the support. The removal of methyl groups creates coordinative unsaturation and leads to the onset of reduction and aggregation of the gold, as evidenced by time-resolved X-ray absorption spectra recorded during the treatment, showing the formation of Au–Au bonds and reduction of the

Au<sup>III</sup> to give supported gold nanoclusters at a temperature approximately the same as that at which the onset of CH<sub>4</sub> formation was observed.

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**Supporting Information Available:** IR spectrum of the sample synthesized by bringing Au(CH<sub>3</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>) in contact with partially dehydroxylated TiO<sub>2</sub> and XANES spectra of gold foil and the TiO<sub>2</sub>-supported sample after treatment in flowing He at 448 K for 2 h. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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