Reactivity and Catalytic Activity of Mononuclear Gold Complexes Dispersed on Supports: Characterization by Time-Resolved X-Ray Absorption Spectroscopy

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Introduction

Bulk gold is one of the least reactive metals and has long been considered to be inactive as a catalyst. However, gold nanoparticles dispersed on metal oxides and zeolites are active catalysts for a number of reactions [1], including CO oxidation, propene epoxidation, and the water-gas shift.

It has been proposed recently that the oxidation states of gold influence its catalytic activity, but, because of the structural complexity of typical supported gold catalysts, and the fact that most investigations on functioning supported gold catalysts have been conducted during steady-state operation, the roles of zerovalent and ionic gold are still not resolved.

There is spectroscopic evidence of the simultaneous presence of cationic and zerovalent gold in some functioning CO oxidation catalysts during steady state operation, and the catalytic activity was correlated with the fraction of gold present as cations in the catalysts [2]. However, there are also reports of CO oxidation catalyzed by samples containing zerovalent gold clusters on supports, in which cationic gold was not detected, and the catalytic activity was explained in terms of the size of the supported gold clusters [3].

In an attempt to investigate the role of cationic gold on CO oxidation catalysis and the influence of the treatment temperature and composition of reactive mixtures on the reduction and aggregation of supported gold, we were motivated to (a) synthesize samples that contained only gold cations in the absence of zerovalent gold during catalysis and (b) follow the decomposition of supported mononuclear (cationic) gold complexes to form supported gold (zerovalent) nanoclusters during treatments at increasing temperature.

Methods and Materials

In the samples syntheses, we used a mononuclear organometallic complex, $Au(CH_3)_2(C_5H_7O_2)$ (dimethyl acetylacetonate Au(III)), and adsorbed it on zeolite NaY and TiO_2 supports. By means of X-ray absorption fine structure (XAFS) and infrared (IR) spectroscopies it was found that adsorption of this complex led to the formation of Au^{III} on both supports.

We recorded time-resolved extended X-ray absorption fine structure (EXAFS), X-ray absorption near edge structure (XANES), and IR spectra of (a) the zeolite-supported sample during CO oxidation catalysis at 298 K and 760 Torr and (b) the TiO_2-supported sample as it was treated in flowing He at increasing temperatures (298-448 K), combined with mass spectra of the evolving gases during the treatments. XAFS and IR spectra were recorded every 2 min.

Results

CO oxidation catalyzed by zeolite-supported gold.

When the initially prepared zeolite-supported sample, containing only Au^{III} complexes, was exposed to a mixture of CO and O_2, catalytic formation of CO_2 occured [4]. Initial CO conversions of approximately 40% were observed when the mass of catalyst was 0.30 g and the total feed flow rate was 100 mL (NTP) min^{-1}. The CO conversion decreased to values < 5% after 15 min time on stream (TOS) and then remained nearly constant. EXAFS spectra recorded during catalysis at steady state give no evidence of Au–Au contributions (Table 1), indicating that the gold remained mononuclear without formation of gold clusters [4]. Time-resolved XANES spectra of the functioning catalyst recorded within the first 15 min TOS show a shift in the absorption edge from 11923.0 ± 0.5 eV, characteristic of Au^{III} present in the initially prepared sample, to 11921.0 ± 0.5 eV, characteristic of Au^{I} and indicative of the reduction of Au^{III} to Au^{I} by the CO + O_2 mixture. The increase in the white line intensity during catalysis (Fig. 1) indicates partial reduction of the gold from Au^{III} to Au^{I}; consistent with these results, there were no XANES features characteristic of Au^{0} detected in the spectrum of the catalyst at any time.

TABLE 1. EXAFS parameters characterizing the zeolite-supported gold catalyst at 298 K. [a]

Treatment gas	Absorber–backscatterer pair	N	R (Å)	$10^3 \cdot \Delta s^2$ (Å^2)	ΔE_0 (eV)
He	Au–Au	[b]	[b]	[b]	[b]
	Au–O	1.9	2.08	4.46	13.02
	Au–Al	1.0	3.20	9.90	-1.05
CO + O_2	Au–Au	[b]	[b]	[b]	[b]
	Au–O	0.47	2.18	-2.13	4.89
	Au–O	1.30	2.79	8.26	-1.06
	Au–Al	0.95	3.25	12.6	-2.52
	Au–C	0.87	1.87	8.52	3.39

[a] Notation: N, coordination number; R, distances between absorber and backscatterer atoms; Δs^2, Debye-Waller factor; DE_0, inner potential correction. Data were obtained with samples in a flow system at steady state. Expected errors: N ± 10%, R, ± 0.02 Å; Δs^2, ± 20%; ΔE_0, ± 20%. [b] Contribution undetectable.

Genesis of supported gold nanoclusters from decomposition of Au^{III} complexes bonded to TiO$_2$.

Time-resolved EXAFS spectra recorded as the initially prepared TiO$_2$-supported sample was treated in flowing He at increasing temperature indicate the presence of mononuclear gold complexes at temperatures lower than about 335 K, as evidenced by the lack of detectable Au–Au contributions [5]. However, when the temperature reached 335 K, the EXAFS spectrum indicated the appearance of a new shell (Fig. 2a), which was fitted with a fractional Au–Au coordination number (Au–Au coordination number < 1) and indicates the start of aggregation of the gold. As the temperature increased further to 390 K, the Au–Au coordination number increased from approximately 0.3 to 5, and then remained nearly constant as the temperature increased to 448 K (Fig. 2a) [5].

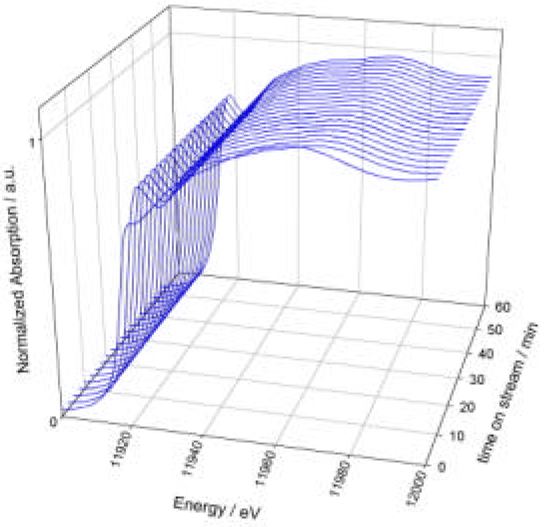

Figure 1. XANES spectra characterizing the sample made by bringing Au^{III}(CH$_3$)$_2$(C$_5$H$_7$O$_2$) in contact with zeolite NaY; data recorded during catalytic oxidation of CO at 298 K and 760 Torr. Feed CO and O$_2$ partial pressures were each 11.7 Torr; total feed flow rate was 100 mL min^{-1} (NTP) and catalyst mass was 0.30 g

XANES spectra recorded during the temperature ramp indicate a continuous decrease in intensity of the white line as the temperature increased from 298 to about 353 K (Fig. 2b). 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 rapidly, being replaced by new peaks at 15 and 25 eV beyond the absorption edge, which are characteristic of Au^0. Simultaneous with these changes, the position of the absorption edge shifted from 11923 to 11919 eV. Finally, the XANES spectrum became indistinguishable from that of gold foil.

These results indicate autoreduction of the initially present Au^{III} to Au^0 as the sample was treated in flowing He at increasing temperatures [5].

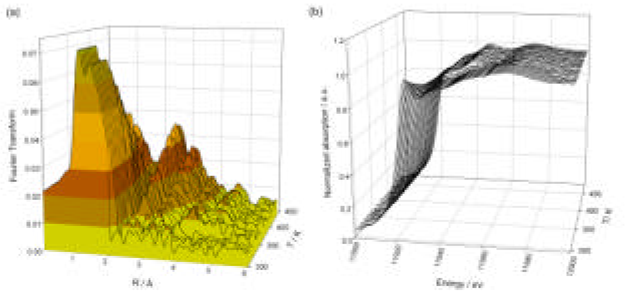

Figure 2. Time-resolved (a) EXAFS and (b) XANES spectra characterizing the formation of gold clusters on TiO$_2$ from the decomposition of supported Au^{III} complexes at increasing temperature.

Discussion

CO oxidation catalyzed by Au^{III} and Au^I complexes bonded to zeolite NaY.

Our results show that the initially present Au^{III} complexes in zeolite NaY are active CO oxidation catalysts. However, the decrease in catalytic activity with increasing TOS suggests that structural *and/or* electronic changes of the supported gold might have taken place during catalysis. Becasue EXAFS spectra show the lack of Au–Au contributions during catalysis, the decrease in catalytic activity is not correlated with aggregation of the gold. In contrast, XANES spectra showing the partial reduction of Au^{III} to Au^I, with a concomitant decrease in catalytic activity, suggest that the changes in the latter were caused by reduction of Au^{III} to Au^I in the absence of Au^0. These results were bolstered by ν_{CO} IR spectra recorded during CO oxidation catalysis and showing bands characteristic of CO bonded to Au^{III} being replaced by bands characteristic of CO bonded to Au^I at increasing TOS [4]. The changes in the intensities of these bands correlate well with the change in CO conversion with TOS and are consistent with the inference that the decrease in catalytic activity was caused by reduction of Au^{III} to Au^I [4]. No ν_{CO} bands characteristic of CO bonded to Au^0 were observed, in agreement with the XANES results, showing no evidence of Au^0.

These results are the first evidence of supported mononuclear cationic gold complexes that are not aggregated and reduced to Au^0 during CO oxidation catalysis [4].

Simultaneous reduction and aggregation of TiO$_2$-supported gold.

Time-resolved EXAFS spectra recorded as the TiO$_2$-supported gold sample was treated in flowing He at increasing temperature show the first formation of Au–Au bonds at about 335 K, as evidenced by the appearance of the Au–Au contribution (Au–Au coordination number < 1) [5]. The Au–Au distance is characteristic of Au–Au bonds in supported gold clusters, and their appearance thus indicates the migration and aggregation of the gold on the TiO$_2$.

The XANES features characteristic of zerovalent gold appeared at a temperature not much higher than 335 K, at which the first formation of Au–Au bonds were observed, suggesting that reduction and aggregation of supported gold are simultaneous processes [5].

We emphasize that the XANES features are indicative of 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. Some unresolved combination of these explains the continuous change in the white line intensity (Fig. 2b), even at temperatures lower than that at which aggregation of the gold started (Fig. 2a).

Summary

Our results show that cationic gold alone (in the absence of Au^0) in zeolite NaY is active for CO oxidation catalysis, and indicate that Au^{III} is more active than Au^I. This is the first example of a supported gold catalyst contaning only gold cations during CO oxidation catalysis, but the activity of this catalyst is lower than that of other catalysts containing mixtures of cationic and zerovalent gold, emphasizing the importance of investigating the processes that lead to the formation of mixtures of cationic and zerovalent gold on supports during catalysis. An approach to this is shown by our results characterizing the formation of gold nanoclusters on the surface of TiO_2 from the decomposition of mononuclear Au^{III} complexes.

Our results are the first showing that the reduction and aggregation of supported gold (or any other metal) occur simultaneously and suggest that by choice of the temperature (as it is our case) or the ratios of reducing and oxidizing reagents (such as CO and O_2 during CO oxidation catalysis) it should be possible to tune the balance between cationic and zerovalent gold—and in prospect the catalytic activity.

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