LETTERS

Mononuclear Au^{III} and Au^{I} Complexes Bonded to Zeolite NaY: Catalysts for CO Oxidation at 298 K

Juan C. Fierro-Gonzalez and Bruce C. Gates*

Department of Chemical Engineering and Materials Science, University of California, Davis, California 95616

Received: August 24, 2004; In Final Form: September 24, 2004

Mononuclear gold complexes in zeolite NaY were synthesized from initially physisorbed Au(CH$_3$)$_2$(C$_5$H$_7$O$_2$) and characterized in reactive atmospheres by X-ray absorption and infrared spectroscopies. Under conditions of CO oxidation catalysis at 298 K and 760 Torr in a flow reactor, the gold remained as mononuclear species, as demonstrated by extended X-ray absorption fine structure spectra indicating the lack of Au−Au contributions. X-ray absorption near edge structure data and infrared spectra in the ν_{CO} region indicate that the initially present Au^{III} was reduced to Au^{I} as the catalyst lost activity during operation in the flow reactor, and the data give no evidence of the formation of clusters of zerovalent gold. The Au^{III} complex is an order of magnitude more active as a catalyst than the Au^{I} complex. These results are the first evidence of supported mononuclear cationic gold complexes as CO oxidation catalysts.

Gold highly dispersed on solid supports is an active catalyst for several reactions, including CO oxidation,[1] propylene epoxidation,[2] and vinyl chloride synthesis.[3] It has been inferred that the oxidation states of gold influence its catalytic activity for CO oxidation[4,5] and the water-gas shift reaction,[6] but because of the structural complexity of typical supported gold catalysts, the roles of zerovalent and ionic gold are still not resolved. X-ray absorption spectra and temperature-programmed reduction and oxidation data[7] indicated the simultaneous presence of both cationic gold and clusters of zerovalent gold (30 Å in diameter, on average) in functioning CO oxidation catalysts supported on MgO.[8] However, there are also reports of CO oxidation catalyzed by samples containing gold nanoclusters with no evidence of gold cations, and the catalysis was explained by size effects of the supported nanoclusters[9] (which are contrasted to single-crystal gold, which adsorbs CO only weakly at temperatures higher than 125 K and catalyzes CO oxidation only after being oxidized itself[10]).

To investigate the role of cationic gold in CO oxidation catalysis, we were motivated to prepare samples containing gold cations in the absence of zerovalent gold. We used a mononuclear organogold complex, Au(CH$_3$)$_2$(C$_5$H$_7$O$_2$) (dimethyl acetylacetonate Au(III)), and adsorbed it on a structurally well-defined (crystalline) support, zeolite NaY; the sample contained 1.0 wt % Au. A similar synthesis route has been used to prepare a mononuclear gold complex on MgO that was active for ethylene hydrogenation.[11] We now report catalytic activity data and spectra showing that either Au^{III} or Au^{I} alone in the zeolite catalyzes CO oxidation.

In the catalyst synthesis, Au(CH$_3$)$_2$(C$_5$H$_7$O$_2$) was physisorbed at 298 K and 760 Torr on zeolite NaY (W. R. Grace and Co.; the support was calcined in O$_2$ at 573 K for 4 h and then evacuated at 10^{-3} Torr at the same temperature for 16 h), as evidenced by infrared (IR) spectra (Supporting Information Figure 1S) showing bands that nearly match those of Au(CH$_3$)$_2$-(C$_5$H$_7$O$_2$) and extended X-ray absorption fine structure (EXAFS) spectra showing that each gold atom was bonded to approximately two oxygen atoms at a distance of 2.08 Å, as in

* To whom correspondence should be addressed. E-mail: bcgates@ucdavis.edu.

TABLE 1: EXAFS Parameters Characterizing the Zeolite-Supported Gold Catalyst at 298 K[a]

treatment gas	absorber−backscatterer pair	N	R (Å)	$10^3 \times \Delta\sigma^2$ (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
O$_2$	Au−Au	b	b	b	b
b	Au−O	0.41	2.21	−5.65	−5.04
	Au−Al	1.26	3.26	7.55	−1.36
	Au−C	0.84	1.92	−0.74	−3.55
CO	Au−Au	b	b	b	b
	Au−O	0.63	2.27	−0.29	−16.03
	Au−Al	1.37	3.31	14.25	−8.60
	Au−C	0.54	1.93	9.28	3.38
CO + O$_2$ during CO oxidation catalysis	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*, distance between absorber and backscatterer atoms; $\Delta\sigma^2$, Debye−Waller factor; ΔE_0, inner potential correction. The data were obtained with samples in a flow system at steady state. Expected errors: *N*, ±10%; *R*, ±0.02 Å; $\Delta\sigma^2$, ±20%; ΔE_0, ±20%. Experimentally determined reference files prepared from EXAFS data representing materials of known structure were used in the analysis. EXAFS data characterizing a gold foil and Na$_2$Pt(OH)$_6$ were used for the phase shifts and backscattering amplitudes of the Au−Au and Au−O$_{support}$ interactions. Au(CH$_3$)$_2$(acac) mixed with SiO$_2$ was used to obtain the phase shifts and backscattering amplitudes for analysis of the Au−C and Au−O interactions. The Au−Al reference file was calculated by using the codes FEFF 7.0 and FEFF 8.0 and structural parameters representing AuAl. [b] Contribution undetectable.
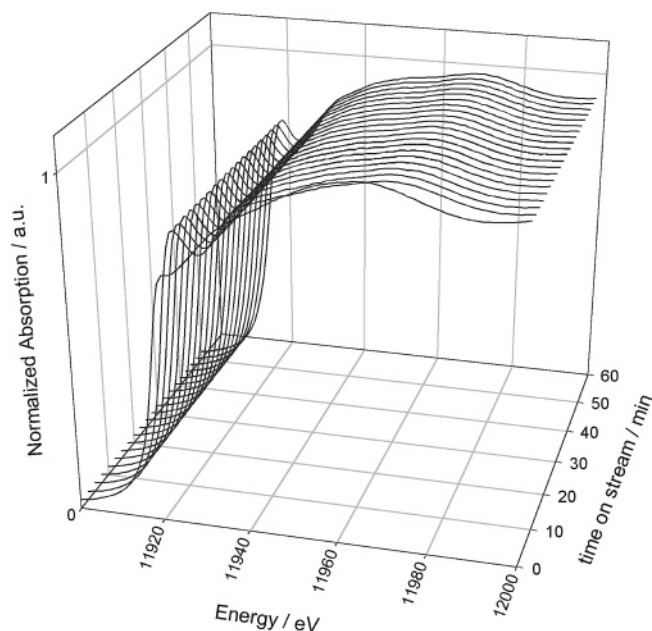

Figure 1. XANES spectra characterizing the sample made by bringing Au^{III}(CH$_3$)$_2$(C$_5$H$_7$O$_2$) in contact with zeolite NaY. The data were recorded during catalytic oxidation of CO at 298 K and 760 Torr. The feed CO and O$_2$ partial pressures were each 11.7 Torr, the total feed flow rate was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

Figure 2. IR spectra characterizing the sample made by bringing Au^{III}-(CH$_3$)$_2$(C$_5$H$_7$O$_2$) in contact with zeolite NaY. The data were recorded during catalytic oxidation of CO at 298 K and 760 Torr. The conditions are the same as those stated in the caption of Figure 1.

Au(CH$_3$)$_2$(C$_5$H$_7$O$_2$) (Table 1). The EXAFS data give no evidence of Au−Au contributions, consistent with isolated mononuclear gold species. The L$_{III}$-edge X-ray absorption near edge structure (XANES) spectrum of the initially prepared sample is consistent with the presence of cationic gold formally represented as Au^{III}, as evidenced by the position of the absorption edge at 11 923 ± 0.5 eV, characteristic of Au^{III}.[8] Although the XANES spectrum of the initially prepared sample has only a barely detectable white line, in contrast to what has been observed for typical complexes containing cationic gold,[12,13] it agrees well with a theoretical XANES spectrum calculated with the FEFF 8.0 code for a model in which a molecule of Au(CH$_3$)$_2$(C$_5$H$_7$O$_2$) is placed close to a fragment of a supercage
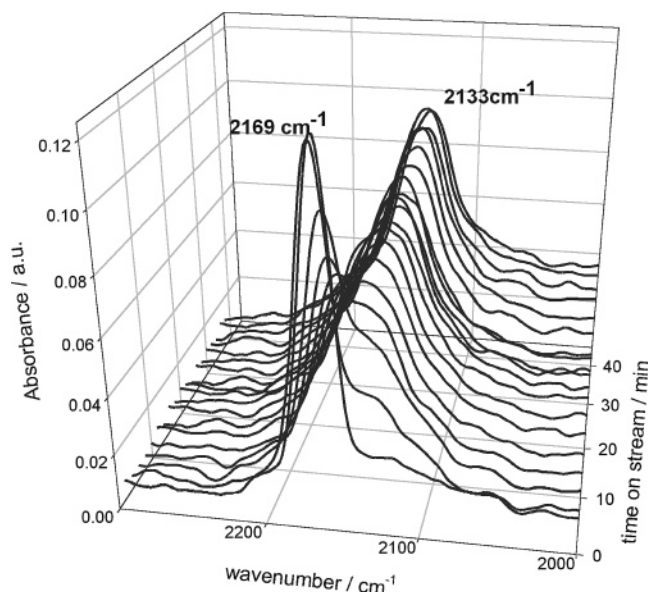
of the zeolite, consistent with the presence of Au^{III} in the initially prepared sample without Au^I or Au^0.[15]

When the initially prepared zeolite-supported sample was exposed to a mixture of CO + O$_2$ ($P_{CO} = P_{O_2} = 11.7$ Torr, in excess He) flowing at 298 K and atmospheric pressure, catalytic formation of CO$_2$ occurred; the support alone was inactive, and therefore, the activity is attributed to the gold. Details of the flow reactor/cell are presented elsewhere.[16] Initial CO conversions of ~40% were observed when the mass of catalyst was the standard (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 of time on stream (TOS) and then remained nearly constant. EXAFS spectra recorded during catalysis[17] at steady state give no evidence of Au−Au contributions, indicating that, within our ability to characterize the gold,[18] it remained mononuclear and site-isolated without the formation of gold
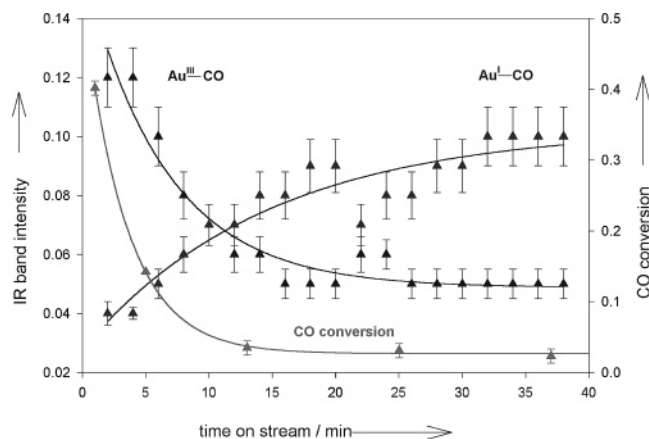
Letters

J. Phys. Chem. B, Vol. 108, No. 44, 2004 **17001**

Figure 3. Dependence of the CO conversion and the intensities of the 2169-cm^{-1} (Au^{III}−CO) and 2133-cm^{-1} (Au^{I}−CO) bands in the IR spectrum of the catalyst during catalytic oxidation of CO at 298 K and 760 Torr. The conditions are the same as those stated in the caption of Figure 1. The units of the IR band intensities are arbitrary.

clusters (Table 1). XANES spectra of the functioning catalyst measured within the first 15 min of TOS show a shift in the absorption edge from 11 923.0 ± 0.5 eV, characteristic of Au^{III} present in the initially prepared sample, to 11 921.0 ± 0.5 eV, characteristic of Au^{I} and indicative of the reduction of Au^{III} to Au^{I} by the CO + O$_2$ mixture; consistent with these results, there were no XANES features characteristic of Au^0 detected in the spectrum of the catalyst at any time.[19] The increase in the white line intensity in the presence of the reactive CO + O$_2$ mixture (Figure 1) demonstrates (a) partial reduction of the gold, (b) a change in the ligand environment of the gold, or (c) both.

These results were bolstered by ν_{CO} IR spectra recorded during CO oxidation catalysis in a flow system; because no ν_{CO} bands were observed in the IR spectra of the bare zeolite, the observed ν_{CO} bands are attributed to CO bonded to the gold. The spectra include no detectable ν_{CO} bands characteristic of CO bonded to Au^0.[20] After a short TOS (prior to recording the first spectrum at 2 min), a band appeared at 2169 cm^{-1}, which we assign to CO bonded to Au^{III} (Figure 2). The intensity of this band decreased with increasing TOS, being almost com-

pletely replaced by a band at 2133 cm^{-1}, which, on the basis of the results stated above, we assign to CO bonded to Au^{I}.[23] The shift of the 2169-cm^{-1} band to lower frequency is consistent with the reduction of Au^{III}; similar trends have been observed for CO on supported cationic Cu[27] and Ag[28] with changes in oxidation states.

Correlations between the intensities of the ν_{CO} bands and the catalytic activity (represented as the conversion of CO) are shown as a function of TOS in Figure 3. The decrease in catalytic activity correlates well with the reduction of Au^{III} to Au^{I}. The latter is an order of magnitude less active than the former at 298 K under our standard reaction conditions.

To understand better the reactions of Au(CH$_3$)$_2$(C$_5$H$_7$O$_2$) physisorbed in the zeolite in the reductive and oxidative atmospheres of CO and O$_2$, respectively, we recorded XANES, EXAFS, and IR spectra of the sample in each of these gases flowing at 298 K and atmospheric pressure. EXAFS results showing how the initially prepared sample changed during reaction with CO and without O$_2$ (P_{CO} = 11.7 Torr and the remainder He; total flow rate of 100 mL (NTP) min^{-1}; standard sample mass) indicate the presence of mononuclear gold in the absence of (zerovalent) gold clusters, as evidenced by the lack of detectable Au−Au contributions. The XANES and IR spectra recorded with the sample in flowing CO show features that match those observed during CO oxidation catalysis (Figure 4a; IR spectra not shown), consistent with the reduction of Au^{III} to Au^{I} without detectable formation of Au^0. A comparison of these results with those stated above shows that CO is a strong enough reducing agent to convert Au^{III} to Au^{I} even in the presence of O$_2$ at the partial pressures used in the catalysis experiments.

In complementary experiments, EXAFS spectra showing the effect on the sample of flowing O$_2$ without CO (P_{O_2} = 11.7 Torr and the remainder He; total flow rate of 100 mL (NTP) min^{-1}; standard sample mass) indicate the presence of mononuclear gold and no gold clusters, as evidenced by the lack of detectable Au−Au contributions. The XANES data recorded during this experiment do not show any significant changes in either the edge position or the white line intensity (Figure 4b), consistent with retention of the mononuclear Au^{III} in the sample, as expected.
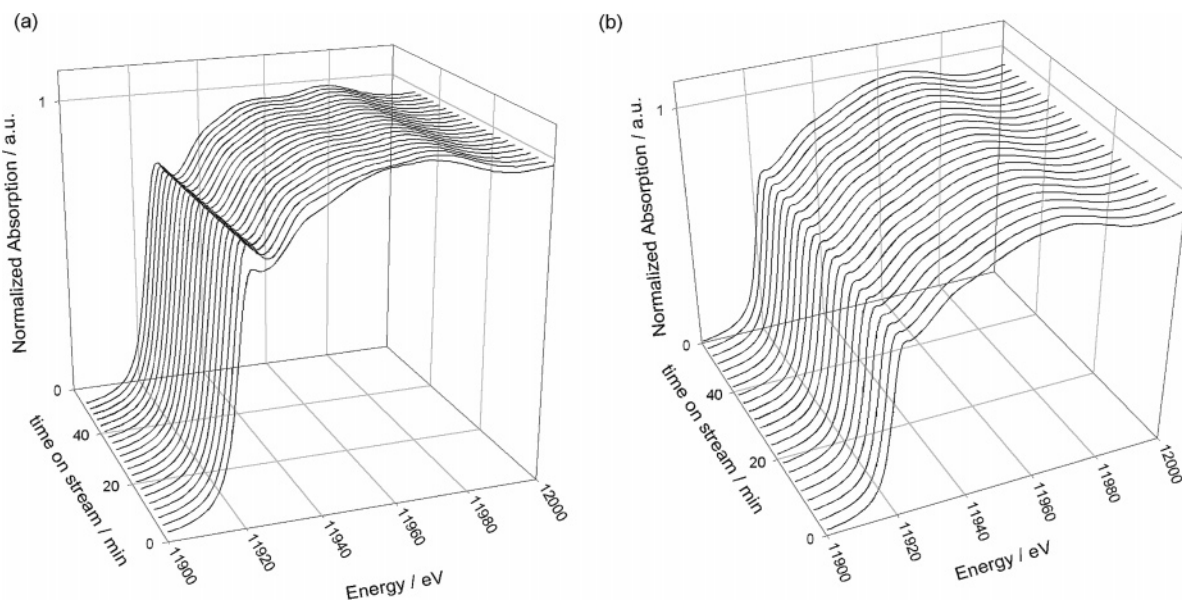

Figure 4. XANES spectra characterizing the sample made by bringing Au^{III}(CH$_3$)$_2$(C$_5$H$_7$O$_2$) in contact with zeolite NaY. The data were recorded with a sample in flowing (a) CO and (b) O$_2$.

Taken together, these results indicate that it is possible to tune the balance of Au^{III} and Au^{I} by selection of the ratio of CO to O_2 in the treatment gas.[29]

In summary, we present the first evidence of a supported mononuclear cationic gold complex catalyst that is not aggregated and reduced to metal during CO oxidation catalysis. The catalyst initially contained only complexes of Au^{III}, which was reduced largely to Au^{I} at a CO partial pressure of 11.7 Torr and an O_2 partial pressure of 11.7 Torr, with an order of magnitude decrease in the catalytic activity. Although we have demonstrated that supported gold cations alone are active for CO oxidation catalysis, we emphasize that our catalysts are less active than some containing mixtures of cationic and zerovalent gold;[31] it remains to be determined how cationic and zerovalent gold interact and influence the properties of typical supported gold catalysts, but one could suggest that Au^0 in nanoclusters might act as a reservoir for adsorbed CO, which could spill over to gold cations at the gold−support interface where catalysis could take place. Similar hypotheses have been suggested by others.[33]

Supporting Information Available: IR spectra of the sample synthesized by bringing $Au(CH_3)_2(C_5H_7O_2)$ in contact with partially dehydroxylated zeolite NaY and plots of EXAFS data indicating comparisons of the data and the fits. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Sanchez, R. M. T.; Ueda, A.; Tanaka, K.; Haruta, M. *J. Catal.* **1997**, *168*, 125.

(2) Stangland, E. E.; Stavens, K, B.; Andres, R. P.; Delgass, W. N. *J. Catal.* **2000**, *191*, 332.

(3) Nkosi, B.; Adams, M. D.; Coville, N. J.; Hutchings, G. J. *J. Catal.* **1991**, *128*, 378.

(4) Bond, G. C.; Thomson, D. T. *Gold Bull.* **2000**, *33*, 41.

(5) Davis, R. J. *Science* **2003**, *301*, 926.

(6) Fu, Q.; Saltsburg, H.; Flytzani-Stephanopoulos, M. *Science* **2003**, *301*, 935.

(7) Guzman, J.; Gates, B. C. *J. Phys. Chem. B* **2003**, *107*, 2242.

(8) Guzman, J.; Gates, B. C. *J. Am. Chem. Soc.* **2004**, *126*, 2672.

(9) Valden, M.; Lai, X.; Goodman, D. W. *Science* **1998**, *281*, 1647.

(10) Outka, D. A.; Madix, R. J. *Surf. Sci.* **1987**, *179*, 351.

(11) Guzman, J.; Gates, B. C. *Angew. Chem., Int. Ed.* **2003**, *42*, 690.

(12) Benfiled, R. E.; Grandjean, D.; Kröll, M.; Pugin, R.; Sawitowski, T.; Schmid, G. *J. Phys. Chem. B* **2001**, *105*, 1961.

(13) The white line at the L_{III} X-ray absorption edge is usually described in terms of electronic transitions from a core level, $2p_{3/2}$, to vacant d states. Numerous theoretical investigations show that in general the intensity of

the white depends not only on the oxidation state(s) of the absorbing metal but also on the geometry of the surroundings of the metal and the identities of the ligands bonded to it.[14]

(14) Bazin, D.; Sayers, D.; Rehr, J. J.; Mottet, C. *J. Phys. Chem. B* **1997**, *101*, 5332.

(15) The only input parameters in the calculation were the coordinates of the absorber and scatterer atoms. Thermal disorder was treated using the Debye model with a Debye temperature of 298 K. Default inputs for the other parameters were used, that is, the Hedin−Lundqvist plasmon−pole self-energy and without any shifts or additional broadening. The card NOHOLE was also used, indicating that the calculations were carried out using initial potentials without a core−hole.

(16) Guzman, J.; Gates, B. C. *J. Phys. Chem. B* **2002**, *106*, 7659.

(17) Ozdak, J. F.; Argo, A. M.; Lai, F. S.; Gates, B. C.; Pandya, K.; Feraria, L. *Rev. Sci. Instrum.* **2001**, *72*, 3943.

(18) The EXAFS spectra were analyzed by a difference file technique embedded in the software XDAP.[34] Multiple coordination shells were added to fit the data, and the number of parameters in the fit was maintained below the justified maximum as determined statistically by the Nyquist theorem. Au−Au contributions were included in the fitting, and the results showed that Au−Au coordination numbers indistinguishable from zero were always found (at either bonding or nonbonding distances). The fitting ranges in both momentum space (k-values from ∼2.1 to ∼14.5) and real space ($0 \leq R \leq 6$) were determined by the data quality, and the quality of the fits was confirmed by the values of fit diagnostic parameters, including ϵ_v^2 (goodness of fit), which was always lower than unity after all the shells had been added in determination of the final fit. Furthermore, the analysis was carried out with the various k-weightings (k^0, k^1, k^2, and k^3) to check for consistency. If Au−Au contributions had been present, they were indistinguishable from the noise in the data in the momentum space range.

(19) The absorption edge characterizing gold foil was observed at 11 919 eV, as expected.

(20) A number of ν_{CO} bands have been assigned to Au^0−CO for various supported gold catalysts: (a) 2110−2120 cm^{-1} for TiO_2-supported gold[21] and HY zeolite-supported gold,[24] (b) 2098−2100 cm^{-1} for γ-Al_2O_3-supported gold.[22]

(21) Boccuzzi, F.; Chiorino, A.; Manzoli, M. *Surf. Sci.* **2000**, *454*, 942.

(22) Winkler, C.; Carew, A. J.; Haq, S.; Raval, R. *Langmuir* **2003**, *19*, 717.

(23) Our assignment of the ν_{CO} bands characterizing CO bonded to cationic gold is supported by the XANES results and is in agreement with reported assignments,[24,25] although the authors did not specify the oxidation state of the gold. Interpretations of other authors[26] differ from ours.

(24) Guillermot, D.; Borovkov, V. Y.; Kazansky, V. B.; Polisset-Thfoin, M.; Fraissard, J. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3587.

(25) Beden, B.; Bewick, A.; Kunimatsu, K.; Lamy, C. *J. Electroanal. Chem.* **1982**, *142*, 345.

(26) Salama, T. M.; Takafumi, S.; Minagawa, H.; Ichikawa, M. *J. Catal.* **1995**, *152*, 322.

(27) Millar, G. J.; Rochester, C. H. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 1477.

(28) Müslehiddinoğlu, J.; Vannice, M. A. *J. Catal.* **2003**, *213*, 305

(29) It is possible to reduce Au^{III} to Au^0 by increasing the partial pressure of CO to 37 Torr at 298 K.[30]

(30) Fierro-Gonzalez, J. C.; Anderson, B. G.; Chathakudath, V. P.; Kanaparthi, R.; Niemantsverdriet, J. W.; Gates, B. C. To be published.

(31) The reaction rate characterizing the catalyst containing Au^{III} was $(2.6 \pm 0.3) \times 10^{-2}$ mol of CO_2 (mol of Au $\times$ s)$^{-1}$, and that characterizing the catalyst containing Au^{I} was $(2.9 \pm 0.2) \times 10^{-3}$ mol of CO_2 (mol of Au $\times$ s)$^{-1}$. For comparison, the most active gold catalyst reported for CO oxidation, gold dispersed on nanocrystalline CeO_2, is characterized by a rate of $(1.60 \pm 0.2) \times 10^{-2}$ mol of CO_2 (mol of Au $\times$ s)$^{-1}$ at 263 K and 760 Torr.[32]

(32) Carrettin, S.; Concepcion, P.; Corma, A.; Lopez Nieto, J. M.; Puentes, V. F. *Angew. Chem., Int. Ed.* **2004**, *43*, 2538.

(33) Haruta, M.; Tsubota, S.; Kobayashi, T.; Kageyama, H.; Genet, M. J.; Delmon, B. *J. Catal.* **1993**, *144*, 175.

(34) Vaarkamp, M.; Linders, J. C.; Koningsberger, D. C. *Physica B* **1995**, *209*, 159.