



CO oxidation catalyzed by gold supported on MgO: Spectroscopic identification of carbonate-like species bonded to gold during catalyst deactivation

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ABSTRACT

MgO-supported gold prepared by adsorption of $\text{Au}(\text{CH}_3)_2(\text{acac})$ (acac is acetylacetonate) on partially dehydroxylated MgO was activated for CO oxidation catalysis by treatment in flowing helium at 473 K. X-ray absorption spectra showed that the activation involved reduction of the gold and formation of clusters (with an average diameter <10 Å) in which the gold was essentially zerovalent. During CO oxidation catalysis in a batch reactor, at least some of the gold was oxidized, as evidenced by the appearance of an $\text{Au}^{\delta+}\text{--CO}$ band at 2151 cm^{-1} in the infrared (IR) spectrum. During operation in a flow reactor, the catalyst underwent deactivation, accumulating species such as carbonate and bicarbonate on its surface, as indicated by IR spectra. The accumulation of such species on the MgO support took place only during the initial period of operation of the catalyst, whereas the accumulation of such species on the gold continued throughout the operation, consistent with the inference that these species blocked catalytically active sites on the gold. The catalyst was reactivated by decomposition of these species by treatment in helium at 473 K. After three activation–deactivation cycles, the average diameter of the supported gold clusters had increased to about 30 Å, and the catalytic activity increased. Thus, the results provide a resolution of the separate effects on the catalytic activity of gold aggregation and accumulation of species such as carbonates and bicarbonates.

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1. Introduction

Samples consisting of gold dispersed on metal oxide supports have been investigated extensively as catalysts for CO oxidation, motivated in large measure by Haruta's discovery [1] that some of these catalysts are highly active, even at temperatures much less than room temperature. Notwithstanding the extensive research, there are still many questions about the nature of the catalytically active sites, the reaction mechanisms, and catalyst deactivation.

The performance of these catalysts is sensitive to the support [2], the catalyst pretreatment conditions [3], the water content of the reactant mixture [4], and components such as chloride, which is present in commonly used precursors such as HAuCl_4 [5]. There is a lack of quantitative results characterizing the performance of supported gold catalysts, which is complicated by the catalyst deactivation.

Deactivation of supported gold CO oxidation catalysts has been ascribed variously to reduction and aggregation of the gold [6,7], other morphological changes in gold clusters [8], and reduction of the support surface [9]. The most commonly suggested causes of

deactivation are sintering of gold clusters [10] and accumulation of carbonate-like species [4,11–13] (carbonates, bicarbonates, carboxylates, and formates). IR spectra of these species on catalyst surfaces are characterized by bands in the $1800\text{--}900\text{ cm}^{-1}$ region, including bands representing $\nu_{\text{asym}}(\text{OCO})$, $\nu_{\text{sym}}(\text{OCO})$, etc. [14].

These deactivation processes may occur simultaneously. For example, Konova et al. [15,16] found evidence of carbonate accumulation and gold agglomeration during CO oxidation catalyzed by Au/ZrO_2 and Au/TiO_2 , observing that the two processes had different effects: sintering of gold caused irreversible deactivation (but the effect was usually small, with most supported gold catalysts retaining their activities as long as the average gold cluster diameter remained within a range of, typically, 2–5 nm); the accumulation of carbonate-like species, on the other hand, may lead to significant activity loss by blocking of active sites, although the effect can be reversed by removal of these species by treatment in inert gas at temperatures up to 573 K.

Deactivation caused by carbonate-like species can also be reversed by other treatments, such as addition of moisture. Kung et al. [17,18] investigated the roles of moisture and of H_2 on $\text{Au/Al}_2\text{O}_3$ catalysts, finding that both were effective in converting carbonate species to reactive formate species (which the authors proposed to be reaction intermediates), with regeneration of the catalyst. Daté

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et al. [4,13] drew a similar conclusion regarding the effect of moisture on Au/Al₂O₃ and Au/TiO₂.

Evidence of build-up of carbonate-like species on catalyst surfaces has emerged from infrared (IR) spectroscopy. The most informative spectra are those characterizing working catalysts, as they may provide correlations between carbonate accumulation and catalytic activity. For example, Shubert et al. [19] claimed that IR spectra gave evidence of carbonate and carboxylate (–COO[–]) species during preferential oxidation of CO in a H₂-containing atmosphere catalyzed by Au/α-Fe₂O₃. As the amounts of these surface species increased with time on stream, the authors inferred that they were responsible for the deactivation. Similarly, Daté et al. [13] observed bands in the carbonate region (at 1435 and 1230 cm^{–1}) during CO oxidation catalyzed by Au/Al₂O₃. The change in intensity of the 1230-cm^{–1} band with time-on-stream correlated inversely with a measure of the catalytic activity for CO₂ formation. When moisture was introduced into feed stream, both bands decreased in intensity and disappeared, and the catalytic activity increased, leading the authors to suggest that carbonate-like species near the active sites caused deactivation.

In work with Au/CeO₂ [20], accumulation of carbonate-like species was indicated by IR bands at 1590, 1440, 1358, and 1270 cm^{–1}. The authors [20] inferred that some of these species were on the support and not the gold—and thus not responsible for the activity loss—whereas the monodentate carbonate species (characterized by the 1358-cm^{–1} band), formed on the support in a reaction with hydroxyl groups and bicarbonate species, did cause deactivation.

To develop a better understanding of the roles of carbonate-like species on supported gold catalysts, especially when the supports are strongly basic and readily form such species from CO and from CO₂ [14,21], our goal was to assess where the species form and whether their formation is influenced by gold. Specifically, we sought to distinguish carbonate-like species on gold and on a strongly basic support; to determine their effects on catalyst performance; and to distinguish the role of these species from that of aggregation of the gold. Thus, we investigated the adsorption of CO and of CO₂ separately on a basic support (MgO) and on Au/MgO. We report characterization of the surface species by IR spectroscopy and simultaneous measurements of the catalytic activity for CO oxidation, as well as characterization of fresh and used catalysts by extended X-ray absorption fine structure (EXAFS) spectroscopy to determine average gold cluster sizes, and by X-ray absorption near edge structure (XANES) spectroscopy to determine gold oxidation state(s). The results provide a basis for separating the effects of the formation of carbonate-like species, cluster growth, and modification of gold oxidation state(s) in the catalyst deactivation; the data demonstrate a correlation between carbonate-like species on gold and catalyst activity loss.

2. Experimental methods

2.1. Materials

He (Airgas, 99.995%) and CO (Airgas, 10% mixture balanced in He, 99.999%) were purified by passage through traps containing reduced Cu/Al₂O₃ and activated zeolite 4A to remove traces of O₂ and moisture, respectively. O₂ (Airgas, 10% in He, 99.999%) was purified by passage through a trap containing activated zeolite 4A to remove traces of moisture. The MgO support (EM Science, 97%, 60 m²/g) was calcined in O₂ at 673 K for 2 h, followed by evacuation at 673 K for 16 h (pressure < 10^{–2} Pa), and stored in an argon-filled glove box until it was used. *n*-Pentane solvent (Fisher, 99%) was dried and purified by refluxing over sodium metal and deoxygenated by sparging of N₂. The catalyst precursor Au(CH₃)₂(acac)

(acac = acetylacetonate, C₅H₇O₂) (Strem, 98%, handled as light- and temperature-sensitive) was used as supplied.

2.2. Catalyst preparation

The synthesis and handling of MgO-supported gold samples were carried out with exclusion of air and moisture on a double-manifold Schlenk vacuum line and in the glove box. Samples were prepared by slurrying Au(CH₃)₂(acac) in dried and deoxygenated *n*-pentane with MgO at 298 K and 10⁵ Pa. The slurry was stirred for 1 day, and the solvent was removed by evacuation for 1 day (pressure < 10^{–2} Pa), giving a sample containing 1.0 wt% Au. The sample was stored in the glove box until used; part of it was sealed under vacuum in glass ampoules for transfer from California to Munich, where IR spectroscopy experiments were carried out in a batch system.

2.3. CO oxidation catalysis and product analysis by mass spectrometry

The as-prepared sample consisting of mononuclear Au(III) complexes bonded to the support [22] was tested at 303 K and atmospheric pressure for CO oxidation catalysis, either with or without pretreatment. The sample (typically, 0.10 g) was loaded into a once-through plug-flow reactor in the glove box and transferred to a flow system without coming in contact with air. In some experiments, the sample was tested for CO oxidation catalysis directly, with the partial pressures of the components in the reactant stream (Pa) being $P_{\text{CO}} = 1520$, $P_{\text{O}_2} = 1520$, and $P_{\text{He}} = 9.83 \times 10^4$. In other experiments, the sample was first treated in flowing helium at 473 K for 4 h and then cooled to 303 K in flowing helium to start the reaction, with the component partial pressures (Pa) being $P_{\text{CO}} = 510$, $P_{\text{O}_2} = 510$, and $P_{\text{He}} = 1.00 \times 10^5$. In the latter experiments (a test of the stability of the catalyst), the cycle of treatment in helium at 473 K followed by CO oxidation catalysis was repeated twice.

During treatment in flowing helium at 473 K and during CO oxidation catalysis, the effluent gases from the reactor were analyzed by mass spectrometry. The on-line instrument was a Balzers OmniStar running in multi-ion monitoring mode. Signals were recorded for the main fragments of CO ($m/e = 28$); O₂ ($m/e = 32$); CO₂ ($m/e = 44$); CH₄ ($m/e = 12, 15, 16$); C₂H₄ ($m/e = 27, 28$); and C₂H₆ ($m/e = 29, 30$). Signals are reported relative to that of the helium carrier gas ($m/e = 4$) to remove effects of small pressure fluctuations during the experiments.

2.4. Temperature-programmed decomposition (TPD)

TPD of the as-prepared sample consisting of mononuclear Au(III) complexes bonded to MgO [22] was carried out in a once-through plug-flow reactor. Helium flowed through the reactor as the temperature was increased from room temperature to 673 K at a rate of 3 K/min. An on-line gas chromatograph (Hewlett-Packard, HP-5890 series II) equipped with a 30-m × 0.53-mm DB-624 (J & W Scientific) capillary column (with N₂ as the carrier gas) and a flame-ionization detector was used to analyze the effluent gases.

2.5. X-ray absorption spectroscopy

Characterization of catalyst samples by X-ray absorption spectroscopy was carried out at beam line X-18B at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL), Upton, NY, and at beam line 10-2 at the Stanford Synchrotron Radiation Laboratory (SSRL) of the Stanford Linear Accelerator Center (SLAC), Menlo Park, CA. The storage ring electron energy was 2.8 GeV at NSLS and 3 GeV at SSRL; the ring current varied within the ranges of 140–300 mA at NSLS and 50–100 mA at SSRL.

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