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Zeolite NaY-supported gold complexes prepared from $Au(CH_3)_2(C_5H_7O_2)$: reactivity with carbon monoxide

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Mononuclear gold complexes in zeolite NaY were synthesized from initially physisorbed $Au(CH_3)_2(C_5H_7O_2)$, and their reactions with CO in a flow system at 298 K and 760 Torr were investigated by infrared (IR) spectroscopy and mass spectral analysis of the effluent gases. CH_4 and CO_2 were formed as CO flowed through the sample either steadily or as successive pulses. The results are consistent with the inferences that (a) CO reacted with the supported gold to form gold carbonyls, (b) CH_4 formed by reaction of methyl groups on gold with traces of H_2O or hydroxyl groups on the zeolite and (c) CO on cationic gold reacted with traces of O_2 and/or H_2O to form CO_2. In samples treated in steadily flowing CO, cationic gold was reduced to zerovalent gold, but the cationic gold in samples exposed to CO pulses was not reduced to zerovalent gold, although CO_2 formed. Thus, CO adsorbed on cationic gold reacts to give CO_2 in the absence of zerovalent gold, consistent with the inference that gold catalysts for CO oxidation need not contain zerovalent gold.

KEY WORDS: catalysis; CO oxidation; DRIFTS; gold catalyst; mass spectroscopy; mononuclear gold complexes.

1. Introduction

The discovery of unanticipated catalytic properties of gold has motivated extensive research in the preceding few years, focused both on (a) soluble mononuclear (cationic) gold complexes (for reactions including selective hydrosilylation of aldehydes [1], addition of alcohols to alkynes [2], and oxidative carbonylation of amines [3], among others [4]) and (b) supported gold (for CO oxidation [5], the water–gas shift reaction [6], and epoxidation of propylene [7], among others [8]).

There is evidence of cationic gold complexes on the surfaces of some of the supported catalysts [9], and cationic gold has been implicated in the catalysis of CO oxidation [10] and the water–gas shift reaction [6]. However, infrared (IR) spectra of functioning supported gold catalysts for CO oxidation indicate CO chemisorbed on both zerovalent and cationic gold [11–19], and it is not yet resolved which oxidation states of gold are responsible for the catalytic activity.

To clarify the roles of cationic gold on supports, we were motivated to prepare supported gold complexes in the absence of zerovalent gold by using a mononuclear organogold complex, $Au(CH_3)_2(C_5H_7O_2)$. This precursor has been used to synthesize MgO-supported mononuclear gold complexes that are catalytically active for ethylene hydrogenation [20]. We now report evidence of the reactivity of cationic gold complexes prepared from physisorption of $Au(CH_3)_2(C_5H_7O_2)$ on a structurally well-defined support, zeolite NaY.

Our goal was to investigate the reactions of CO with $Au(CH_3)_2(C_5H_7O_2)$ and the species formed from it on the zeolite. We report measurements of diffuse reflectance Fourier transform infrared (DRIFT) spectra of the surface species and mass spectra of the evolved gases. The sample powder was treated with (a) CO flowing at steady state and (b) CO pulsed through the sample – to allow characterization of stepwise changes in the supported species resulting from contact with only small amounts of CO.

Our results provide evidence of the formation of CO_2 resulting from the reaction of the physisorbed gold precursor with CO at 298 K and 760 Torr and show that, by addition of pulses of CO to the sample, it is possible to avoid reduction of the initially present gold cations to zerovalent gold.

2. Experimental

Sample syntheses and transfers were performed in the absence of air and moisture on a double-manifold Schlenk vacuum line and in a glove box purged with Ar that was recirculated through traps containing particles of supported Cu and zeolite 4A for removal of O_2 and moisture, respectively. The sample, containing 1.0 wt% Au, was prepared by slurrying $Au(CH_3)_2(C_5H_7O_2)$ (Strem, 98%) in *n*-pentane at 298 K with zeolite NaY powder (W. R. Grace and Co.) that had been calcined in

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flowing O_2 and then dried under vacuum at 573 K. The slurry was stirred for 2 days and the solvent removed by evacuation (pressure $< 10^{-3}$ Torr) for 1 day. Samples were loaded into the DRIFT cell inside a dry box containing an Ar atmosphere (moisture and oxygen levels were ca. 1 ppm). The cell was closed and isolated with two standard two-way vacuum valves, removed from the dry box, and remounted in the spectrometer. Spectra were recorded with a resolution of 4 cm^{-1} with a Nicolet Protégé^{TM} FTIR spectrometer equipped with a SpectraTech Collector^{TM} DRIFT attachment fitted with a high-temperature environmental chamber; they were transformed by using the Kubelka-Munk function. Spectra were recorded by coadding 256 scans (unless otherwise stated). KBr powder was normally used as a reference material.

DRIFT spectra were recorded as each sample (ca. 25 mg) was treated in either steadily flowing CO (P_{CO} = 36 Torr, with the remainder He; total flow rate 11 mL (NTP) min^{-1}) or with a sequence of pulses of CO (4 μmol per pulse at an interval 60 s) at 298 K and 760 Torr (thus, the amount of CO coming in contact with the sample per unit time in steadily flowing CO was approximately 5-times as great as the average amount of CO coming in contact with the sample in the pulse experiments). Ultrahigh purity He (Hoekloos, 99.9999%) and high-purity CO (Matheson, 99.9%) were used. The flow rate of each gas was controlled with a mass flow controller (Brooks).

Mass spectra of the effluent gases from the reactor/DRIFTS cell were measured with an on-line Balzers OmniStar^{TM} mass spectrometer running in multi-ion monitoring mode. The changes in the signal intensities of the main fragments of H_2 (m/e = 2), CH_4 (m/e = 12, 13, 14, 15, 16), H_2O (m/e = 16, 17, 18), CO (m/e = 12, 14, 16, 28), O_2 (m/e = 16, 32), and CO_2 (m/e = 16, 28, 30, 44) were recorded. Because several of those components have fragments with signals at m/e = 16, the analysis characterizing CH_4 was carried out by following the changes in intensity of the signal at m/e = 15, as this signal was unique for CH_4. All signals are reported relative to that of the He carrier gas at m/e = 4 to remove any effects of pressure fluctuations. Although ultrahigh purity He and high-purity CO were used and purified with traps, the sensitivity of the mass spectrometer was such that ppm levels of both O_2 and H_2O could be detected in these gases.

3. Results

3.1. Evidence of physisorption of $Au(CH_3)_2(C_5H_7O_2)$ in the calcined zeolite

IR spectra characterizing the sample synthesized by bringing $Au(CH_3)_2(C_5H_7O_2)$ in contact with calcined zeolite NaY show bands at 1537, 1463, and 1384 cm^{-1} that nearly match those observed in the spectrum of crystalline $Au(CH_3)_2(C_5H_7O_2)$ (figure 1), indicating that the organogold precursor was initially physisorbed in the zeolite [21].

3.2. Formation of CO_2 and CH_4 upon CO treatment of the zeolite-supported gold sample

Mass spectra of the effluent gases from the flow reactor/DRIFTS cell when the sample was treated in

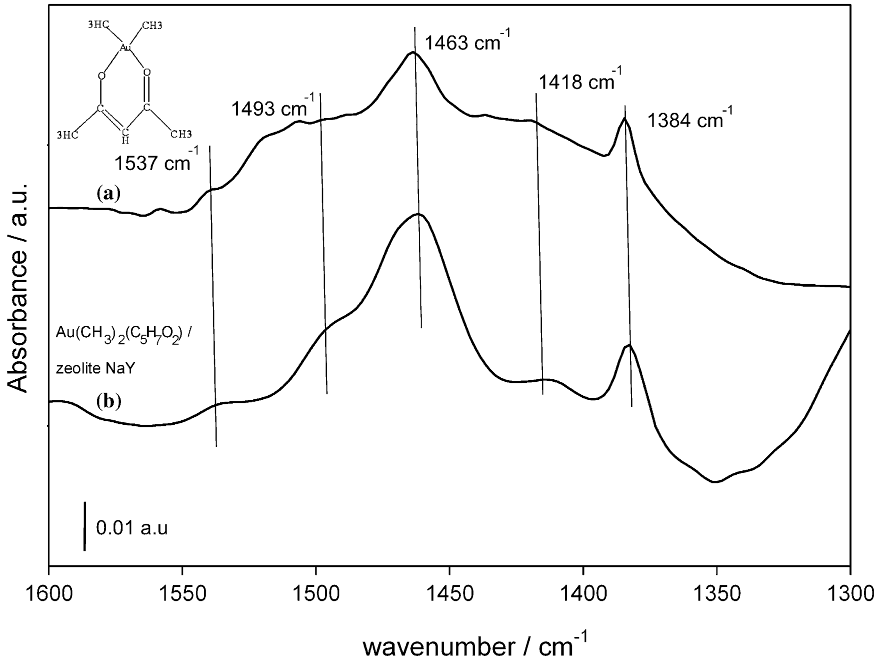

Figure 1. IR spectra characterizing (a) crystalline $Au(CH_3)_2(C_5H_7O_2)$ and (b) the sample made by bringing $Au(CH_3)_2(C_5H_7O_2)$ in contact with calcined zeolite NaY.

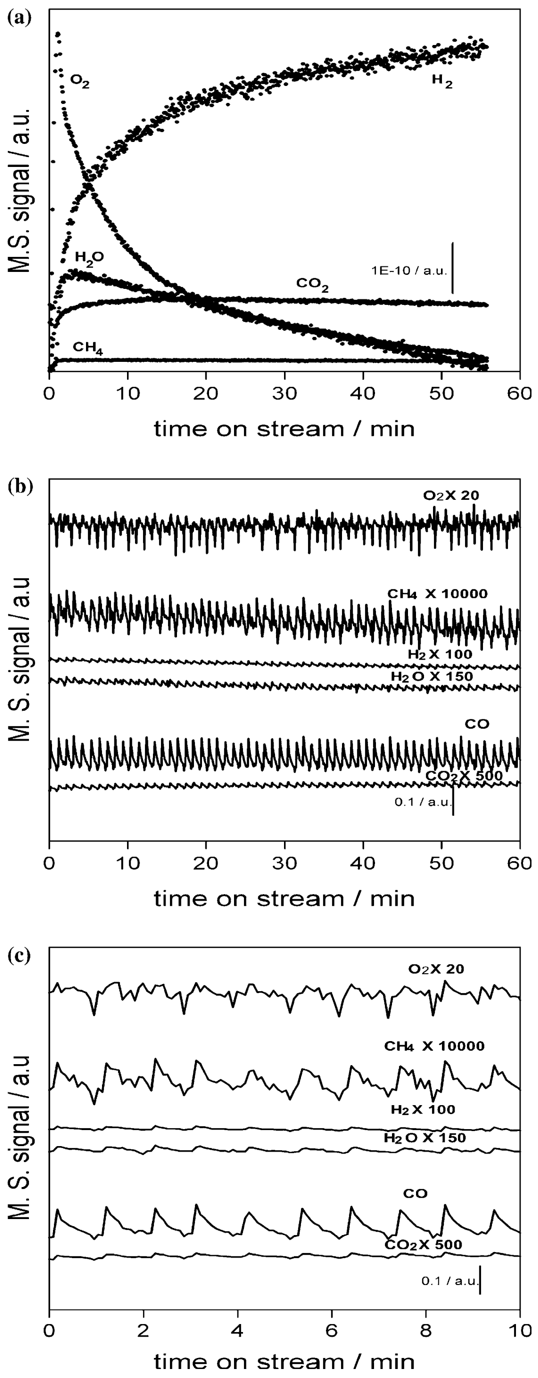

Figure 2. Changes in the intensity of the mass spectral signals of the effluent gases from the flow reactor/DRIFTS cell when the sample made by bringing $Au(CH_3)_2(C_5H_7O_2)$ in contact with calcined zeolite NaY was treated in (a) steadily flowing CO (P_{CO} = 36 Torr, with the remainder He; total flow rate 11 mL (NTP) min^{-1}) and (b) CO pulses (4 μmol per pulse at an interval 60 s) at 298 K and 760 Torr. (c) Changes in the mass spectral signals during the first 10 CO pulses shown in figure 2b.

either steadily flowing CO or with consecutive pulses of CO indicate formation of CO_2 (m/e = 44) and CH_4 (m/e = 15) (figure 2). H_2 was also detected in the effluent gas mixture. Steady state was not attained even after the sample had been treated for 1 h in steadily flowing CO (figure 2a). Analysis of the effluent pulses by mass spectrometry showed that the formation of CO_2 was accompanied by the depletion of CO and O_2 (figure 2b and c), as evidenced by the appearance of a positive CO_2 peak and a negative O_2 peak with the concomitant decrease in the intensity of the signal characterizing CO. These results indicate that CO was oxidized by traces of O_2 in the feed.

3.3. *DRIFT spectra characterizing removal of organic ligands from zeolite-supported gold sample during CO treatment*

IR spectra of the initially prepared sample as it was treated in steadily flowing or pulsed CO showed a decrease in intensity of the ν_{CH} bands at 2868, 2930, and 2960 cm^{-1} with increasing time on stream (TOS); simultaneously, the ν_{OH} bands at 3683, 3740, 3410 and 3240 cm^{-1} increased in intensity (figure 3). These results indicate the removal of ligands containing C–H groups from the surface.

IR spectra of the sample in steadily flowing or pulsed CO in the 1600–1300 cm^{-1} region did not undergo significant changes with increasing exposure to CO, suggesting that the acetylacetonate groups introduced with the precursor remained essentially intact, but bands appeared at 1685 and 1737 cm^{-1} during exposure to CO, characteristic of formate groups [22] (figure 4).

3.4. *DRIFT spectra characterizing formation of gold carbonyls bonded to zeolite when initially prepared sample was treated in CO*

IR spectra recorded when CO was fed to the originally prepared sample (either steadily or in pulses) demonstrate the appearance of ν_{CO} bands, indicating the reaction of $Au(CH_3)_2(C_5H_7O_2)$ with gas-phase CO to give gold carbonyls. Bands at 2178 and 2169 cm^{-1} (figures 5 and 6) appeared within 1 min, prior recording of the first IR spectrum during the treatment. Thereafter, these bands decreased in intensity during continued exposure to CO and were replaced by bands at 2070, 2032, and 2000 cm^{-1} (figure 5). Furthermore, a very broad band, with some visible fine structure and centered at approximately 2140 cm^{-1}, was observed to increase in intensity. On the basis of reports [12–18] of IR spectra of CO adsorbed on supported gold (table 1), which show that ν_{CO} bands representing CO adsorbed on zerovalent gold appear at lower wavenumbers than those characterizing CO adsorbed on cationic gold (for which wavenumbers are generally higher than approximately 2130 cm^{-1}), we assign the bands at 2169 and 2178 cm^{-1} to CO adsorbed on cationic gold [23] and those at 2070, 2032, and 2000 cm^{-1} to the non-degenerate C–O stretching modes of low-symmetry (C_1) $Au^0(CO)_3$ complexes formed on zerovalent gold clusters [24]. The decrease in intensity of the 2169- and 2178-cm^{-1} bands and the appearance of the 2070-,

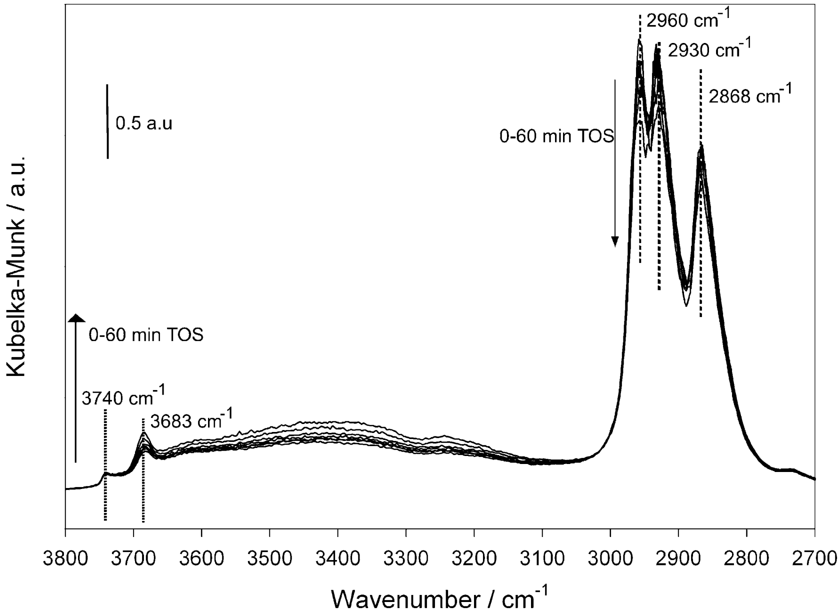

Figure 3. ν_{CO} and ν_{CH} DRIFT spectra characterizing the sample prepared by bringing $Au(CH_3)_2(C_5H_7O_2)$ in contact with calcined zeolite NaY as it was treated in steadily flowing CO during 60 min. Conditions as stated in caption of figure 2.

2032-, and 2000-cm^{-1} bands with increasing TOS indicate reduction of the initially present cationic gold to zerovalent gold when the sample was treated in steadily flowing CO.

The plot of figure 7 shows how the intensities of the 2169- and 2032-cm^{-1} bands are correlated. These results show how fast the cationic gold initially present in the supported sample prepared from $Au(CH_3)_2(C_5H_7O_2)$ (in which the gold is formally Au^{III}) was reduced to zerovalent gold in steadily flowing CO at 298 K and 760 Torr.

In contrast, the spectra of the sample recorded after successive pulses of CO show ν_{CO} bands only at 2169 and 2178 cm^{-1} (figure 6), and these both increased in intensity with an increasing number of CO pulses (figure 6). Furthermore, a very broad band, with some visible fine structure and centered at approximately 2140 cm^{-1}, was observed to increase with increasing

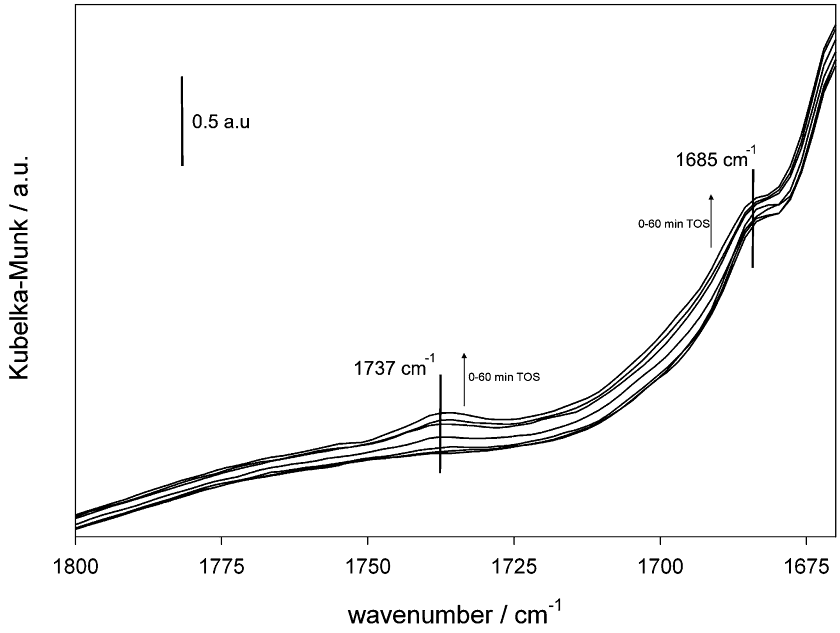

Figure 4. IR spectra showing the appearance of bands characteristic of formate groups when the sample made by bringing $Au(CH_3)_2(C_5H_7O_2)$ in contact with calcined zeolite NaY was treated in steadily flowing CO during 60 min. Conditions as stated in caption of figure 2.

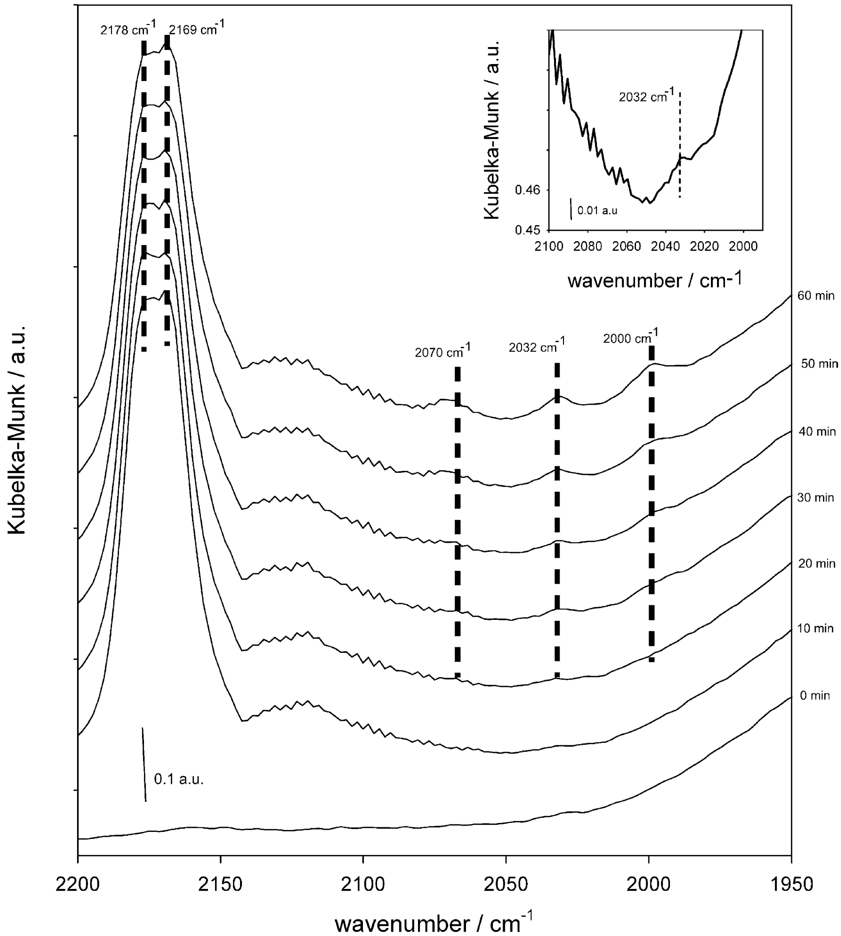

Figure 5. IR spectra in the ν_{CO} region characterizing the sample made by bringing $Au(CH_3)_2(C_5H_7O_2)$ in contact with calcined zeolite NaY as it was treated in steadily flowing CO (conditions as stated in caption of figure 2). Inset: IR spectra representing the sample treated in flowing CO after 10 min TOS.

number of CO pulses (figure 6); no other ν_{CO} bands were observed in these experiments, even after 60 pulses of CO. These results show that the gold was not reduced to the zerovalent state when the sample was treated with pulses of CO, in contrast to the results observed when CO flowed steadily through the sample.

In blank experiments, the procedures described above were carried out under the same conditions with NaY zeolite that contained no gold. No bands were observed in the ν_{CO} region. However, a band at 1640 cm^{-1}, characteristic of molecular H_2O, appeared, and its intensity increased with increasing TOS, consistent with the presence of traces of H_2O in the feed; these traces of H_2O were confirmed by mass spectra of the feed gas.

4. Discussion

4.1. Reactions of $Au(CH_3)_2(C_5H_7O_2)$ physisorbed in zeolite NaY with CO and traces of H_2O and O_2

The results reported here for the reactions of $Au(CH_3)_2(C_5H_7O_2)$ physisorbed in zeolite NaY with CO indicate the formation of CH_4 and CO_2 in the gas phase. The CH_4 might be thought to have arisen from the decomposition of acetylacetonate groups; however, because the IR spectra in the ν_{COO} region characterizing the sample in the presence of CO show that the acetylacetonate bands remained essentially unchanged (consistent with reports [25,26] showing that decomposition of other metal acetylacetonate complexes to give CH_4 does not occur at a significant rate at room temperature), we conclude that the source of gas-phase CH_4 is other than the decomposition of acetylacetonate groups.

Instead, CH_4 might arise from reaction of the methyl groups on the gold with traces of H_2O present in the feed. To test this hypothesis, the CH_4 formation as detected by the mass spectrometer and the changes in intensities of the ν_{CH} bands in the IR spectra recorded for the sample in steadily flowing CO are plotted as a function of TOS in figure 8. The decline in the rate of formation of CH_4 with increasing TOS is correlated with the decrease in concentration of methyl groups on the sample surface. The decrease in intensity of the ν_{CH} bands is also correlated with the increase in

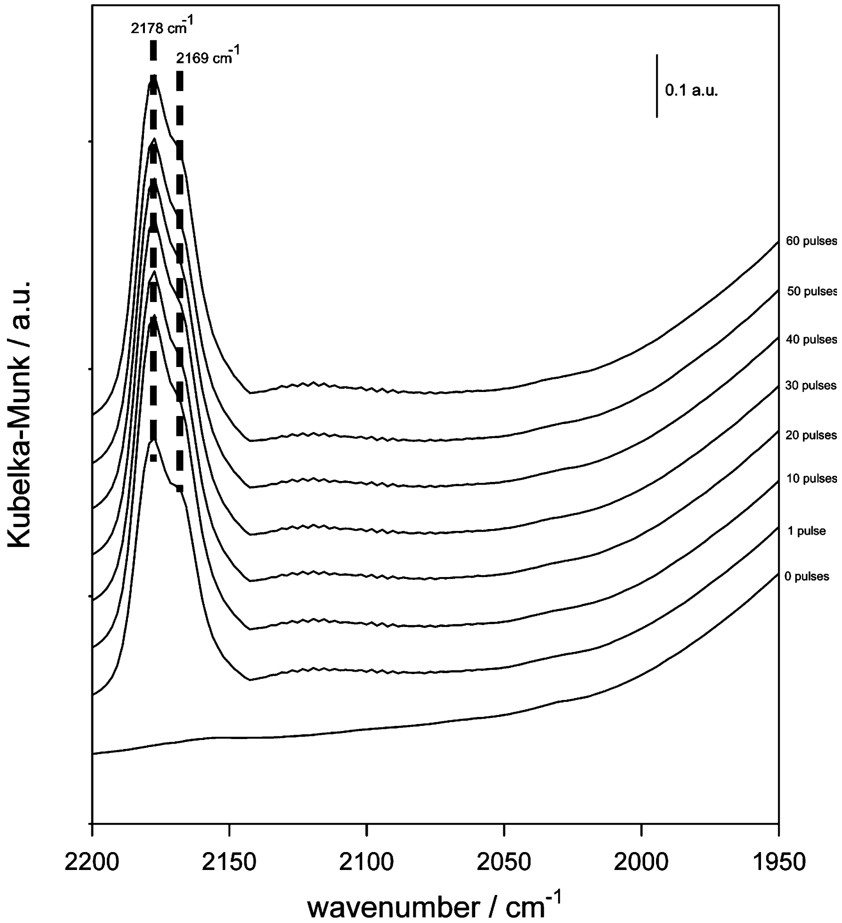

Figure 6. IR spectra in the ν_{CO} region characterizing the sample made by bringing $Au(CH_3)_2(C_5H_7O_2)$ in contact with calcined zeolite NaY as it was treated with a sequence of pulses of CO (4 μmol per pulse; pulse interval = 60 s) at 298 K and 760 Torr.

intensity of the ν_{OH} bands in the IR spectra (figure 9), consistent with the hypothesis of a reaction between methyl groups on gold and traces of H_2O in the feed stream to give gas-phase CH_4 and hydroxyl groups on the zeolite surface [27].

The possibility that CO_2 formed by the decomposition of acetylacetonate groups is discounted on the basis of the IR spectra, which show no changes in the ν_{COO} region, as described above. Instead, the appearance of IR bands characteristic of formate ligands (figure 4)

Table 1
Assignments of ν_{CO} bands in IR spectra of supported gold samples

Sample	ν_{CO}/cm^{-1}	Assignment	Reference
Au/TiO_2	2140–2160	CO on Au^{I}	[12]
	<2130	low coordinated Au^0	[12]
	2155	CO interacting by H-bonding with hydroxyl groups on TiO_2	[13]
Au/HY zeolite	2111–2122	CO linearly adsorbed on Au^0	[14]
	2169, 2172	CO adsorbed on oxidized gold	[14]
	2138–2142	CO linearly adsorbed on $Au^{\delta+}$	[14]
Au/NaY zeolite	2169	CO adsorbed on Au^{III}	[15]
	2133	CO adsorbed on Au^{I}	[15]
	2192	CO adsorbed on Au^{I}	[16]
	2128	CO adsorbed on Au^0	[16]
Au/ZrO_2	2108	CO adsorbed on Au^0	[17]
	2140	CO adsorbed on positively charged gold clusters	[17]
Au/SiO_2	2112	CO adsorbed on Au^0	[18]
NaY zeolite	2170–2174	Na^+–CO	[19]
	2163	Na^+–$(CO)_2$	[19]
	2120	Na^+–OC	[19]

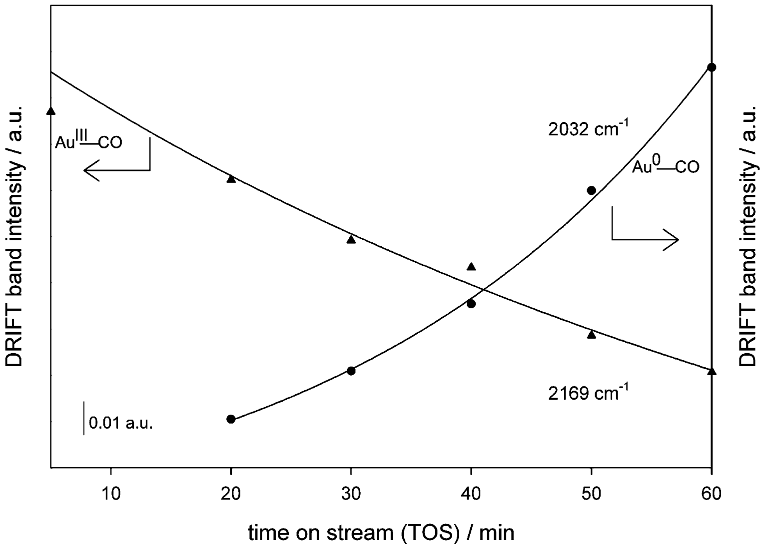

Figure 7. Correlation between the intensities of the bands at 2169 cm^{-1} (triangles) and 2032 cm^{-1} (circles) as a function of TOS characterizing the sample made by bringing $Au(CH_3)_2(C_5H_7O_2)$ in contact with calcined zeolite NaY as it was treated in steadily flowing CO. Conditions as stated in caption of figure 2.

suggests that CO adsorbed on gold could be involved in the formation of CO_2, because formate ligands are typical products of the reaction of CO adsorbed on supported metals with either O_2 or H_2O, even in trace amounts [28] (Formate ligands have been proposed to be reaction intermediates in both CO oxidation and the water–gas shift reaction catalyzed by supported gold [22]). Mass spectra characterizing the products when the sample was treated with pulses of CO show that the formation of CO_2 is correlated with the consumption of CO and O_2 (figure 2c). However, it is unclear whether CO from the gas phase reacted with O_2 traces to give CO_2 (which is unlikely at 298 K and 760 Torr, as evidenced by the lack of CO_2 formation when the bare zeolite was exposed to CO under the same conditions) or whether gold carbonyls were involved in the formation of CO_2. To test whether the gold carbonyls were precursors for the formation of CO_2, a measure of the CO_2 formation as detected by mass spectrometry and the change in intensities of the ν_{CO} bands in the IR spectra recorded for the sample in steadily flowing CO are plotted as a function of TOS in figure 10. At short TOS (<1 min), when only the bands at 2169 and 2178 cm^{-1} (characterizing CO bonded to cationic gold) had appeared in the ν_{CO} spectra, the formation of CO_2 increased to a maximum, and then it declined as the

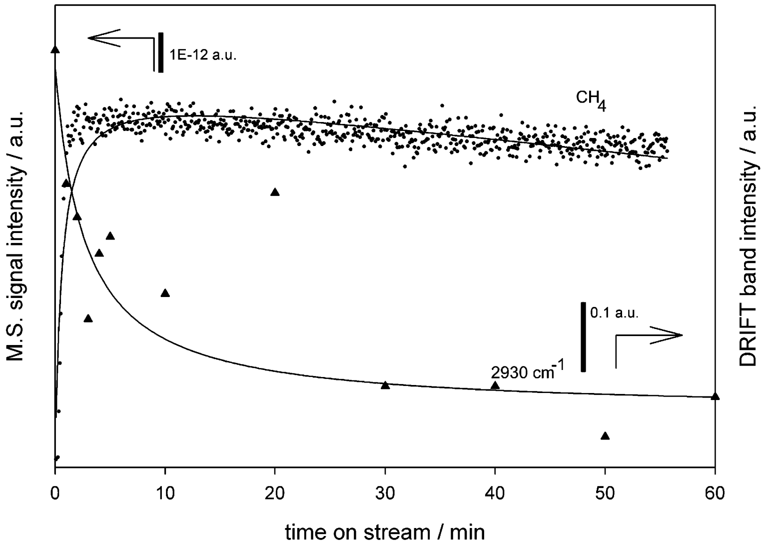

Figure 8. Correlation between the intensity of the mass spectral signal characterizing the formation of CH_4 (m/e = 15; circles) and the intensity of the IR band at 2930 cm^{-1} (triangles) as a function of TOS for the sample made by bringing $Au(CH_3)_2(C_5H_7O_2)$ in contact with calcined zeolite NaY as it was treated in steadily flowing CO. Conditions as stated in caption of figure 2.

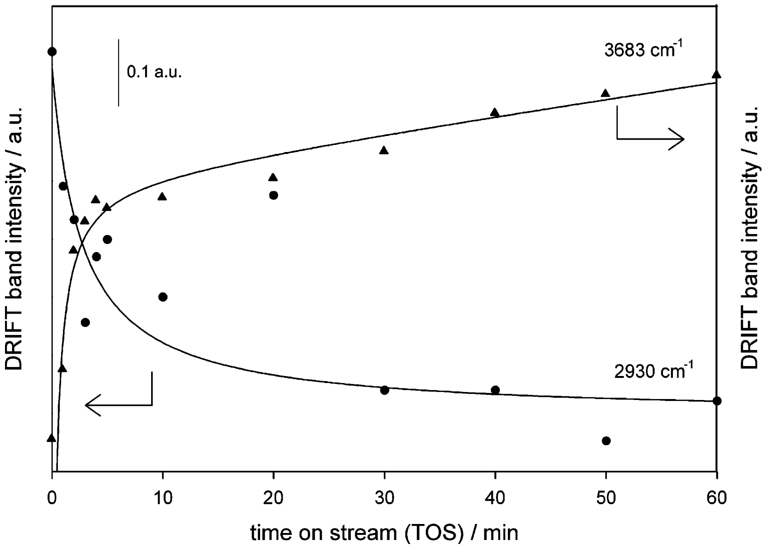

Figure 9. Correlation between the intensities of the bands at 3683 cm^{-1} (triangles) and 2930 cm^{-1} (circles) as a function of TOS characterizing the sample made by bringing $Au(CH_3)_2(C_5H_7O_2)$ in contact with calcined zeolite NaY as it was treated in steadily flowing CO. Conditions as stated in caption of figure 2.

intensities of the 2169- and 2178-cm^{-1} bands decreased and ν_{CO} bands characterizing CO bonded to zerovalent gold appeared and grew in. Therefore, we conclude that the CO_2 initially formed arose from the reaction of CO bonded to cationic gold with traces of O_2 and/or H_2O present in the feed. The results also suggest that the decrease in the rate of formation of CO_2 after the maximum was caused by reduction of the initially present cationic gold to zerovalent gold (although we cannot rule out an effect of decreasing surface area of zerovalent gold clusters as a result of aggregation).

We lack sufficient data to explain the appearance of two distinct bands (at 2169 and 2178 cm^{-1}) rather than a single peak, representing CO adsorbed on cationic gold. As shown in table 1, IR bands have been observed in this region for CO adsorbed on Na^+ ions in NaY zeolite in the presence of gas-phase CO. However, no bands were observed on the parent NaY zeolite under the conditions of our experiments, and we therefore discount this possibility.

The nature of the broad band that was observed to increase with time at ca. 2140 cm^{-1}, because of the appearance of fine structure, might seem to indicate the C–O stretching mode of gaseous CO (normally observed at 2143 cm^{-1}). However, this band appeared with the sample in both steadily flowing and pulsed CO (figures 5

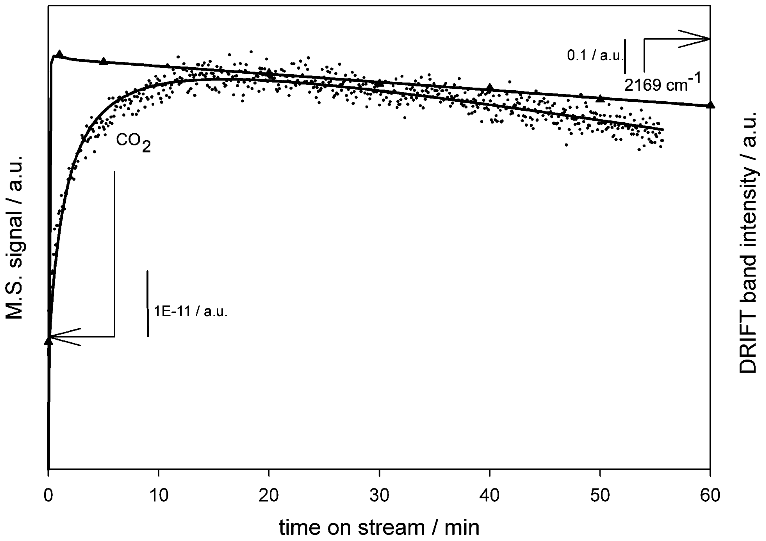

Figure 10. Correlation between the intensity of the mass spectral signal characterizing the formation of CO_2 (m/e = 44; circles) and the intensity of the IR band at 2169 cm^{-1} (triangles) as a function of TOS for the sample made by bringing $Au(CH_3)_2(C_5H_7O_2)$ in contact with calcined zeolite NaY as it was treated in steadily flowing CO. Conditions as stated in caption of figure 2.

and 6). In the latter case the partial pressure of CO in the He stream became negligible between pulses, and so we reject gas-phase CO as the source of this band. Band fine structure may also be observed when very weak adsorption occurs. As shown in table 1, a band was observed between 2138 and 2142 cm^{-1} for CO on gold in HY zeolite. This band was assigned [14] to CO on $Au^{\delta+}$ ions interacting with protons. It might indicate some partial reduction of gold in our samples, perhaps associated with the hydroxyl groups that were also observed to increase in concentration with time.

4.2. *Lack of reduction of cationic gold in zeolite-supported gold sample treated with pulsed CO*

IR spectra characterizing the sample treated in CO pulses show that the initially present cationic gold was not reduced to zerovalent gold, as evidenced by the absence of ν_{CO} bands characteristic of CO bonded to zerovalent gold; CO_2 formation (at an approximately constant rate) was observed (figure 2b) after each pulse.

These results show that CO added in pulses to $Au(CH_3)_2(C_5H_7O_2)$ physisorbed in zeolite NaY reacts to form gold carbonyls, as evidenced by the appearance of ν_{CO} IR bands at 2178 and 2169 cm^{-1}, which then react with either traces of O_2 or H_2O to give CO_2 without reduction of the cationic gold to zerovalent gold. These results suggest that the formation of CO_2 is not necessarily accompanied by the reduction of cationic gold when CO is added in small, discrete amounts. Although the total amount of CO that was fed to the sample after 60 pulses of CO is equivalent to that fed after approximately 11 min TOS for the sample treated in steadily flowing CO, reduction of cationic gold to zerovalent gold had occurred within 10 min TOS in the latter case, as evidenced by the appearance of a distinguishable (but small) peak at 2032 cm^{-1} characterizing CO bonded to zerovalent gold in the IR spectra (figure 5, inset). However, when the sample was treated with pulsed CO, the partial pressure of CO was negligible during significant periods between pulses. Therefore, conditions in this case were not as reductive as those during treatment under steadily flowing CO. It is possible that as CO_2 formed when the sample was treated in pulses of CO, other ligands (perhaps hydroxyl groups from the support or from traces of water) coordinated to the gold in the absence of competition from CO in the feed, minimizing the reduction of cationic gold after each pulse. In contrast, when the sample was treated in steadily flowing CO, there was always CO available in the gas phase to coordinate to the gold once CO_2 had been desorbed, and because CO is a reducing agent, cationic gold was reduced to zerovalent gold at increasing TOS.

4.3. *Implications for CO oxidation catalysis*

These results have implications for oxidation of CO catalyzed by supported gold: (a) they suggest a role of water influencing the oxidation state of gold, consistent with literature reports of the role of water influencing the catalysis [29,30], and (b) they point to the possibility of catalysis of this reaction by cationic gold in the absence of zerovalent gold, consistent with recent spectroscopic evidence [15]. The results also highlight the importance of traces of water and oxygen in the reactions of supported gold.

5. Conclusions

In summary, the data show that $Au(CH_3)_2(C_5H_7O_2)$ physisorbed in zeolite NaY reacts with steadily flowing or pulsed CO to produce CH_4 and CO_2 in the gas phase. The results suggest that CH_4 was probably formed by reaction of methyl groups on the gold with traces of H_2O in the feed stream. Our results provide evidence of the formation of CO_2 from reaction of CO adsorbed on supported cationic gold complexes with traces of O_2 and/or H_2O, with the concomitant reduction of cationic gold to zerovalent gold in steadily flowing CO. In contrast, when the CO was added in pulses, the gold remained unreduced although CO_2 still formed.

Acknowledgments

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