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Gas-phase studies of $Au_nO_m^+$ interacting with carbon monoxide

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This paper is dedicated to Professor Tilmann Märk on the occasion of his 60th birthday.

Abstract

The results of reactions between preformed cationic gold oxide clusters and carbon monoxide have been investigated utilizing a fast-flow reactor mass spectrometer. From these studies, it was found that all $Au_nO_m^+$ produced in the cluster source disappeared with CO addition at the reactant gas inlet. Furthermore, with CO addition, intermediate peaks of the form $Au_nO_m(CO)_x^+$ ($n = 1$–2, $m = 0$–3, $x = 0$–2) were produced, with some of the species continuing to react at higher CO flows.

Keywords: CO oxidation; Gold cluster; Cluster reaction; Gas phase

1. Introduction

Carbon monoxide oxidation has been an area of extensive research of late [1–4], with its conversion to CO_2 encompassing numerous practical applications [5]. Therefore, is has become necessary to find a suitable catalyst to promote this reaction. The oxidation of carbon monoxide in the presence of gold cluster ions has been investigated both on supports and in the gas phase [5–15]; interest in this area has been prompted, in part, by the findings of Haruta et al. [5,14,15] who have found that supported gold clusters can effect the catalytic oxidation of carbon monoxide. There have been some studies in both supported as well as the gas state on the reactions of anionic species [6–13], but the effect of charge state on this reaction has not been extensively studied. There exist a few reports on the limited activity of gas-phase gold cations for reactions between CO and oxygen with Au_n^+ [16,17]. However, recent reports from Kung and coworkers propose a reaction mechanism in which supported gold cations take part in the catalytic oxidation of CO [18–20]. Furthermore, various other studies propose that gold cations at the metal-support interface play a unique role in catalytic reactions [8,21]. Therefore, it is thought that active sites consisting of charged gold centers may be the answer to gold's ability in catalyzing various reactions [22,23].

It has been reported that gas-phase clusters may function as models for the "cluster-like" assemblies of atoms on catalytic surfaces, thus providing complimentary information to surface science studies [24,25]. This suggestion has prompted the investigations, reported herein, of the reactions between preoxidized gas-phase gold cluster cations and carbon monoxide, with the goal of facilitating the further understanding of the role of charge state on the mechanisms involved in the oxidation of CO by gold.

2. Experimental details

These studies were performed utilizing a fast-flow reactor mass spectrometer, which has been discussed in detail previously [26–28]. Briefly, preoxidized gold cluster cations are produced in a laser vaporization source by passing oxygen seeded in helium over the metal plasma formed from the ablation of a gold rod. Carbon monoxide in increasing amounts is introduced to the preoxidized gold cluster cations via a reactant gas inlet which is located downstream of the cluster source. Most of the species and the buffer gas are pumped off by a high volume roots blower, but the surviving species are sampled through a 1-mm orifice and analyzed by a quadrupole mass spectrometer. The products are subsequently detected utilizing a channel electron multiplier.

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3. Results and discussion

Here we present results for the oxidation of CO in the presence of gold cluster cations in the gas phase. Due to the method of oxygen introduction, we observe gold oxide species in which oxygen is bound in both the molecular and atomized forms to Au^+ and $Au_2{}^+$. This allows for the CO oxidation reactions to be performed on these small cationic species. Our results for the oxidation of CO in the presence of the gas-phase atomic anion have been reported previously [28]. Briefly, we found that AuO^- and $AuO_3{}^-$ promote the oxidation reaction. This conclusion was reached based on the decreasing intensity or the disappearance of the gold oxides coupled with the increase in intensity of the bare atomic gold anion. However, the production of CO_2 was not observed in any of the studies due to the inability to detect neutral species. In contrast, we observe that all of the preoxidized gold cluster cations formed in our cluster source react with the CO added at the reactant gas inlet. Furthermore, species of the form $Au_nO_m(CO)_x{}^+$, where $n = 1$–2, $m = 0$–3, and $x = 0$–2, are produced upon CO addition. Some of these species then continue to react with higher CO flows as discussed below. Typical reaction spectra are shown in Fig. 1.

These spectra are for 1–2% oxygen seeded in helium at the source and 0–50 sccm (standard cubic centimeters per minute) of 0.3% CO in helium added downstream at the reactant gas inlet. From these spectra, it is seen that with increasing CO addition the gold oxide species of the form $Au_nO_m{}^+$, which are preformed in the source, decrease in intensity, and in some cases, they completely disappear. Moreover, in successive spectra, intermediate product peaks appear and either increase in intensity or continue to react.

The further reactions of the intermediate $Au_nO_m(CO)_x{}^+$ species are particularly interesting observations. Examples of these reactions are presented in Fig. 1a for AuO_2CO^+ and more dramatically for AuO_3CO^+. As observed, upon CO addition, the peak corresponding to AuO_2CO^+ gradually decreases in intensity, while that of AuO_3CO^+ appears to practically disappear. With higher CO flow rates (not shown for the sake of not overcomplicating the mass spectrum), these peaks continue to disappear. The same trend is observed to occur for Au_2CO^+ and Au_2OCO^+ with the disappearance dominating over the appearance of the peak at flow rates near 50 sccm (0.3%) CO. (cf. Fig. 1b) A summary of the behaviors of the various peaks with CO addition is given in Table 1.

The trends presented in Table 1 show that all of the species of the form $Au_nO_m{}^+$ decrease in intensity, and most of the peaks disappear with CO addition. Furthermore, intermediate peaks appear and either undergo further reaction or remain constant. For instance, $AuCO^+$ increases upon initial CO addition but decreases with higher CO flows, and while it is evident that a reaction is taking place, it is not clear what this species is reacting to form. Another example, $Au(CO)_2{}^+$, reacts away upon further CO addition, but $Au(CO)_3{}^+$ is not observed in the mass spectrum; therefore,

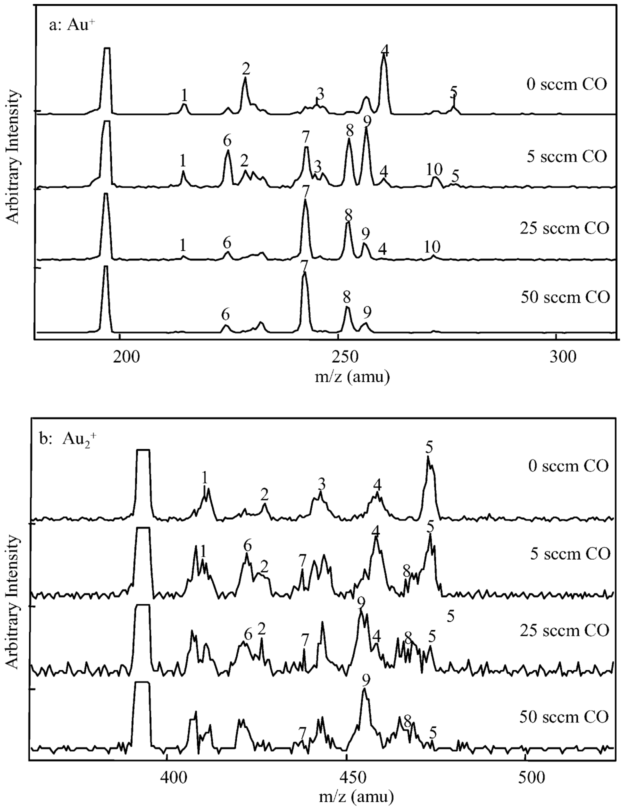

Fig. 1. Reactions of CO with (a) $AuO_y{}^+$ and (b) $Au_2O_y{}^+$. Top spectra in each represent oxygen introduced at the source, and successive spectra are for increasing amounts of CO added at the reactant gas inlet. The peaks are labeled as follows: (a) (1) AuO^+, (2) $AuO_2{}^+$, (3) $AuO_3{}^+$, (4) $AuO_4{}^+$, (5) $AuO_5{}^+$, (6) $AuCO^+$, (7) $AuOCO^+$, (8) $Au(CO)_2{}^+$, (9) AuO_2CO^+, (10) AuO_3CO^+; (b) (1) Au_2O^+, (2) $Au_2O_2{}^+$, (3) $Au_2O_3{}^+$, (4) $Au_2O_4{}^+$, (5) $Au_2O_5{}^+$, (6) Au_2CO^+, (7) Au_2OCO^+, (8) $Au_2O(CO)_2{}^+$, (9) $Au_2O_2CO^+$.

Table 1
Behavior of peaks with co addition

Species	Behavior upon initial CO addition	Behavior upon further CO addition
AuO^+	↓	d
$AuO_2{}^+$	↓	d
$AuO_3{}^+$	↓	d
$AuO_4{}^+$	↓	d
$AuO_5{}^+$	↓	d
$AuCO^+$	↑	↓
$AuOCO^+$	↑	rc
$Au(CO)_2{}^+$	↑	↓(sl)
AuO_2CO^+	↑	↓
AuO_3CO^+	↑	↓, d
Au_2O^+	↓(sl)	↓
$Au_2O_2{}^+$	↓	d
$Au_2O_3{}^+$	↓	d
$Au_2O_4{}^+$	↓	↓
$Au_2O_5{}^+$	↓	↓
Au_2CO^+	↑	d(s)
Au_2OCO^+	↑	d(s)
$Au_2O(CO)_2{}^+$	↑	rc
$Au_2O_2CO^+$	↑(sl)	↑, rc

↓: decreases; ↑: increases; d: disappears; (sl): slight; rc: remains constant; (s): slow.

$Au(CO)_2^+$ does not simply add another CO molecule. There are also a few species which either remain constant or continue to increase in intensity with further CO addition. As an example, $Au_2O(CO)_2^+$ increases in intensity with initial CO addition, and then the intensity remains constant. $Au_2O_2CO^+$, however, continues to increase in intensity with higher flows of CO.

4. Conclusion

These results for the reactions between carbon monoxide and gas-phase gold clusters display significant differences in the reaction mechanisms which arise due to charge state. From the studies reported herein and more extensive experimental and theoretical investigations of the atomic anion [28], we find the following results. All preformed cationic gold oxides decrease in intensity and disappear with CO addition, while AuO^- and AuO_3^- are the only atomic anion species to promote the oxidation reaction [28]. Furthermore, intermediate peaks of the form $Au_nO_m(CO)_x^+$ are produced with CO addition, but no intermediates are observed in the anion studies [28]. Moreover, with further CO addition, some intermediate peaks undergo further reactions in the cation studies.

The preliminary data presented herein are promising, and with continuing experimental and theoretical investigations, more insight into the mechanisms and the nature of the active site on gold catalysts will be obtained.

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