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Strongly cluster size dependent reaction behavior of CO with O_2 on free silver cluster anions

Liana D. Socaciu, Jan Hagen, Jérôme Le Roux, Denisia Popolan, Thorsten M. Bernhardt,[a] and Ludger Wöste
Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

Štefan Vajda
Argonne National Laboratory, Chemistry Division, Argonne, Illinois 60439

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Reactions of free silver anions Ag_n^- ($n=1-13$) with O_2, CO, and their mixtures are investigated in a temperature controlled radio frequency ion trap setup. Cluster anions Ag_n^- ($n=1-11$) readily react with molecular oxygen to yield $Ag_nO_m^-$ ($m=2$, 4, or 6) oxide products. In contrast, no reaction of the silver cluster anions with carbon monoxide is detected. However, if silver cluster anions are exposed to the mixture of O_2 and CO, new reaction products and a pronounced, discontinuous size dependence in the reaction behavior is observed. In particular, coadsorption complexes $Ag_n(CO)O_2^-$ are detected for cluster sizes with $n=4$ and 6 and, the most striking observation, in the case of the larger odd atom number clusters Ag_7^-, Ag_9^-, and Ag_{11}^-, the oxide product concentration decreases while a reappearance of the bare metal cluster signal is observed. This leads to the conclusion that carbon monoxide reacts with the activated oxygen on these silver clusters and indicates the prevalence of a catalytic reaction cycle. © *2004 American Institute of Physics.*
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The variation of physical and chemical characteristics over orders of magnitude by addition or removal of a single atom is the most fascinating property of matter in the cluster state. In the nonscalable size regime,[1] below about 100 atoms per particle, free silver clusters show strong odd–even size alternations in their electronic properties. A great deal of experimental and theoretical effort has been devoted to the elucidation of these interesting physical properties of isolated silver clusters.[2,3] Considerably less is known about the *chemical* properties of small free silver clusters. However, the cluster electronic structure is expected to be reflected in the chemical functionality of silver clusters. This could already be confirmed in some cases.[4–7] Such gas phase cluster reaction studies under well defined conditions support the understanding of catalytic reaction processes, in particular because the finite and limited size of these systems enables detailed direct treatment by *ab initio* theoretical calculations.

Silver with μm particle size is used commercially in large scale as oxidation catalyst in the ethylene epoxidation process.[8] However, nothing is known so far about the capabilities of atomic silver clusters to act as oxidation catalysts. The reactions of neutral and positively charged silver clusters with oxygen have been investigated previously.[5,6,9] In particular, our group observed temperature dependent molecular and dissociative adsorption of oxygen on Ag_2^+, demonstrating the propensity of silver clusters to activate the oxygen molecular bond.[5] An earlier report treating the reaction of negatively charged silver clusters with oxygen showed that odd size cluster anions with even valence electron number exhibit about an order of magnitude smaller reaction rates than even size cluster anions.[4] The same paper also reports that silver clusters are unreactive toward carbon monoxide.[4] A recent theoretical study provides evidence that the odd size silver cluster anions Ag_3^- and Ag_5^- are able to activate the oxygen molecular bond due to cooperative effects in the adsorption of two O_2 molecules.[10] The theoretical binding energies of $Ag_nO_m^-$ ($n=1-5, m=2,4$) are in accord with our measured oxidation rate constants of these cluster sizes.[10]

In the present Communication, we extend our reaction study to larger cluster sizes and to reactions of Ag_n^- with O_2 as well as CO. Silver oxide cluster products formed under multicollision conditions from Ag_n^- ($n=1-11$) in a radio frequency (rf)-ion trap setup will be presented. The aim of this investigation is to identify the final product species of the reactions of these clusters with oxygen which are then to be key intermediates in many catalytic reactions with silver oxide clusters involved. Furthermore, it will be shown that particular silver oxide complexes react with carbon monoxide and the implications on the catalytic activity and size dependent chemical functionality of silver cluster anions will be discussed.

The guided ion beam technique employed in the present investigation is a well established method in gas phase cluster chemistry.[2,11] The instrument comprises cluster generation by sputtering of metal targets and mass-selection as well as ion guidance via quadrupole techniques. Our experimental approach to investigate metal cluster reactions consists in storing the mass-selected cluster ions in an rf-octopole ion trap filled with about 1 Pa of helium buffer gas and small partial pressures of reactant gases. Temperature control inside the trap between 20 and 300 K is achieved with a helium-cryostat attached to the trap enclosure. The initial cluster concentration is defined by the space charge limit

[a]Author to whom correspondence should be addressed. Electronic mail: tbernhar@physik.fu-berlin.de

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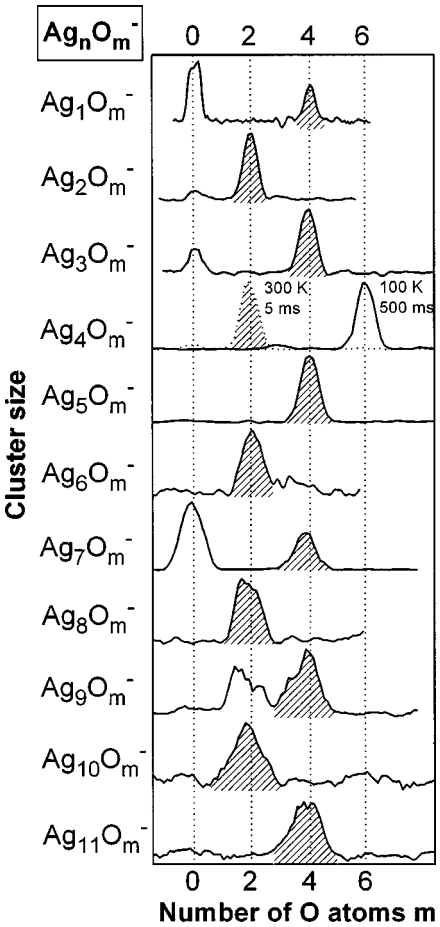

FIG. 1. Product ion mass spectra after reaction of Ag_n^- with O_2. Ion signals are plotted as a function of the number of oxygen atoms in the corresponding metal cluster complexes. $Ag_nO_2^-$ and $Ag_nO_4^-$ peaks are hatched to illustrate the alternation with odd and even n. Reaction temperature in all cases $T_R = 100$ K, except for Ag_2^-, and for Ag_4^- (dotted line) $T_R = 300$ K. Ag_1^-: $p_{O_2} = 0.07$ Pa, $p_{He} = 1.05$ Pa, $t_R = 5$ s. Ag_2^-: $p_{O_2} = 0.12$ Pa, $p_{He} = 1.06$ Pa, $t_R = 0.5$ s. Ag_3^-: $p_{O_2} = 0.06$ Pa, $p_{He} = 1.03$ Pa, $t_R = 1$ s. Ag_4^- (dotted line): $p_{O_2} = 0.01$ Pa, $p_{He} = 1.03$ Pa, $t_R = 0.005$ s. Ag_4^- (solid line): $p_{O_2} = 0.01$ Pa, $p_{He} = 1.04$ Pa, $t_R = 0.5$ s. Ag_5^-: $p_{O_2} = 0.01$ Pa, $p_{He} = 1.03$ Pa, $t_R = 0.5$ s. Ag_{6-11}^-: $p_{O_2} = 0.01$ Pa, $p_{He} = 1.17$ Pa, $t_R = 0.1$ s.

(10^4 ions per mm^3). After defined reaction, i.e., storage time t_R of a few milliseconds up to seconds, the product ions are extracted from the trap and mass-analyzed. Details of this setup have been described previously.[5]

To study the catalytic propensities of small silver cluster anions, first, the reactions of Ag_n^- (n=1–13) with oxygen only were investigated. For Ag^- to Ag_5^- the cluster source intensity was high enough to allow a cluster size preselection before entering the ion trap as reported previously.[10] For the larger sizes ($n \geqslant 6$) a preselection was not possible due to small cluster current and the reactions of a narrow cluster size distribution were measured. Figure 1 displays mass spectra taken at 100 K under different reaction conditions, i.e., different oxygen partial pressures p_{O_2} and different reaction times t_R, in order to achieve comparable intensities of reaction products for different cluster sizes. The cluster complexes belonging to the peak at the largest mass, i.e., the maximum number of oxygen atoms in the complex (Fig. 1), always represent the final reaction product. No larger oxide clusters have been observed for the cluster sizes up to $n = 11$. It can be seen that all investigated clusters Ag_n^- ($n = 1-11$) exhibit a measurable reactivity with O_2. The Ag_{12}^- signal was relatively small and disappeared completely upon reaction with oxygen, but no oxide products could be unambiguously identified in this case. Ag_{13}^- does not appear to react with oxygen at all as the metal cluster signal decreased only weakly when oxygen was present in the trap and no oxide products could be observed.

The interesting odd–even trend reported earlier for $Ag_nO_m^-$ ($n = 1-5, m = 2,4,6$) extends to larger cluster sizes as can be seen from the mass spectra in Fig. 1: Clusters with an even number of silver atoms adsorb one O_2 molecule, while the odd sized clusters, including the monomer, adsorb up to two O_2 molecules. An exception is Ag_4^- which first forms $Ag_4O_2^-$ (300 K, short reaction time, cf. Fig. 1), but then reacts farther with up to three O_2 (100 K, cf. Fig. 1)

$$Ag_n^- + O_2 \rightarrow Ag_nO_2^- \quad (n \text{ even}),$$

$$Ag_4O_2^- + 2O_2 \rightarrow Ag_4O_6^-,$$

$$Ag_n^- + 2O_2 \rightarrow Ag_nO_4^- \quad (n \text{ odd}).$$

No oxide products with an odd number of oxygen atoms have been detected, in agreement with the earlier reports.[4,10]

The results of the oxygen reaction experiment (cf. Fig. 1) can be rationalized qualitatively by considering the frontier orbital structure of the cluster adsorbate complexes:[4,10] Taking into account the highest occupied orbital of the silver cluster, which is either singly (even n) or doubly (odd n) occupied, and the fact that molecular oxygen will interact with the cluster through one of its degenerate unpaired electrons in the $2p\pi^*$ antibonding orbitals, always an even number of valence electrons (closed shell) is acquired for $Ag_nO_4^-$ (n odd) and for $Ag_nO_2^-$ (n even). This result confirms the strong influence of the electronic structure on cluster complex stability in the case of atomic silver clusters.

We furthermore observe an increase in silver cluster anion reactivity toward O_2 with increasing size. Again in agreement with earlier experiments,[4,10] this increase shows a significant odd–even alternation in the reactivity with the even size clusters (open shell clusters with odd number of valence electrons) being more than one order of magnitude more reactive than odd size clusters. Reaction kinetics could be measured for Ag^- to Ag_5^-. An evaluation of the kinetics and absolute rate constants for these clusters together with a detailed analysis of this striking odd–even size dependence based on *ab initio* calculations are given in a separate publication.[10] For the larger sizes ($n \geqslant 6$), the reactions proceed too fast to be resolved in our experiment. Trace amounts of O_2, which are below the sensitivity of our Baratron pressure gauge (<0.01 Pa), are sufficient to completely oxidize the even numbered clusters with $n \geqslant 6$ within a few hundred milliseconds.

Interestingly, the sequential adsorption of two oxygen molecules on the odd size clusters takes place without appearance of intermediate products $Ag_nO_2^-$ in the product ion mass spectra recorded at various reaction times. An exception is Ag_9^-, where $Ag_9O_2^-$ could be detected (cf. Fig. 1).

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This demonstrates that the adsorption of the first O_2 is the rate limiting step in these reactions, whereas the secondary O_2 addition must proceed within the Langevin collision rate limit[12] or at least on a much faster time scale than the resolution of our experiment.

Finally, all reactions studied display increasing rate constants with decreasing temperature. Hence, the mass spectra in Fig. 1 are observed under fastest reaction conditions at 100 K. This negative temperature dependence is indicative for barrierless adsorption pathways.[13] A similar behavior has been found for the reactions of small gold cluster anions Au_n^- with O_2 and CO.[14,15] This is, however, in marked contrast to our previous investigation of the oxidation mechanism of positively charged silver dimer Ag_2^+, where distinct reaction barriers and temperature dependent reaction pathways could be observed.[5]

In a second step, we studied the reactivity of silver cluster anions with solely carbon monoxide in the trap. For Ag^- to Ag_3^- no reactions were observed between 100 and 300 K within the detection limit of our experiment, while for Ag_4^- and Ag_5^- to a small extent fragmentation of the clusters (10% after $t_R = 10$ s, 100 K) could be measured. For larger sizes no adsorption of CO onto the clusters or any new cluster compounds were detected as well. Due to the above mentioned difficulty to preselect the larger clusters, a fragmentation of the clusters after the interaction with CO cannot be entirely excluded. Also in the earlier investigation no reaction products of silver cluster anions with carbon monoxide were reported.[4]

The carbon monoxide combustion reaction

$$2CO + O_2 \rightarrow 2CO_2,$$

although exothermic by 283 kJ/mol,[16] does not proceed in the gas phase under ambient conditions due to a high activation energy barrier, which mainly results from the necessity to break the oxygen molecular bond. To tackle the question whether atomic silver cluster anions might be able to activate the O_2 bond and to act as oxidation catalysts we investigated this model type reaction. For this purpose the clusters were exposed to a mixture of O_2 and CO (and helium) in the ion trap. The surprising results are as follows: For Ag^- to Ag_3^- no new reaction products besides the known oxides $Ag_nO_m^-$ (see Fig. 1) were detected over the whole temperature range between 100 and 300 K. For Ag_4^-, at low oxygen partial pressure p_{O_2} and high carbon monoxide partial pressure p_{CO}, a new peak in the product ion mass spectrum could be identified at 100 K. The mass spectrum is depicted in Fig. 2(a) and the hatched peak corresponds to the species $Ag_4(CO)O_2^-$. In this case, preadsorption of O_2 onto the cluster apparently promotes subsequent CO coadsorption. This phenomenon of cooperative coadsorption has been described previously in the case of gold cluster anions Au_n^-,[17] in particular for Au_2^-, where $Au_2(CO)O_2^-$ was identified as an intermediate in the catalytic CO oxidation cycle on Au_2^-.[14]

A representative product ion mass spectrum of Ag_5^- reacting with both, O_2 and CO, is displayed in Fig. 2(b). Additional peaks arising from fragmentation can be assigned to $Ag_4O_6^-$, $Ag_3O_4^-$, $Ag_3CO_2^-$, and Ag_3^-. No coadsorption of CO and O_2 onto Ag_5^- was observed, but the various fragments indicate that a variety of still unidentified reactions proceed when both reactant molecules are present. The fragment ion $Ag_3CO_2^-$ even points toward a possible reaction between CO and O_2 involved with the metal cluster decomposition. Figure 2(c) shows the mass spectrum recorded after Ag_6^- to Ag_8^- reacted with oxygen and carbon monoxide in the ion trap. Coabsorption is detected for Ag_6^-, yielding the species $Ag_6(CO)O_2^-$.

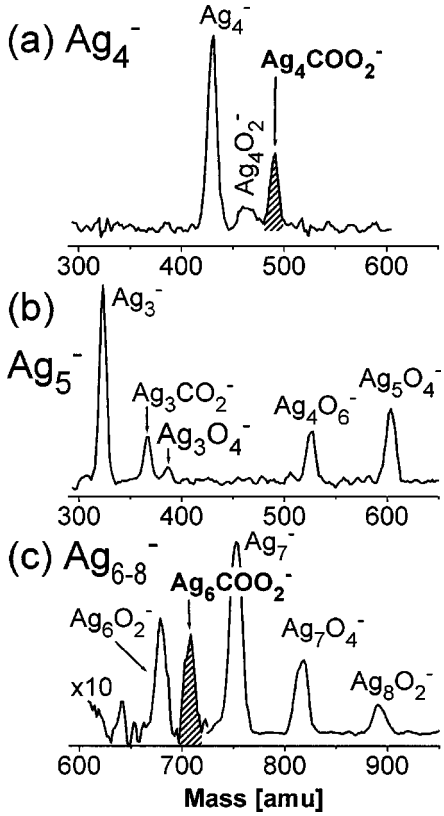

FIG. 2. Product ion mass spectra after reaction of Ag_{4-6}^- with O_2 and CO at $T_R = 100$ K. (a) Ag_4^-: p_{O_2} = trace amounts, $p_{CO} = 0.03$ Pa, $p_{He} = 1.25$ Pa, $t_R = 2$ s. (b) Ag_5^-: $p_{O_2} = 0.01$ Pa, $p_{CO} = 0.03$ Pa, $p_{He} = 1.23$ Pa, $t_R = 1$ s. (c) Ag_{6-8}^-: $p_{O_2} = 0.01$ Pa, $p_{CO} = 0.03$ Pa, $p_{He} = 1.17$ Pa, $t_R = 0.1$ s.

For the larger sizes Ag_n^- ($n = 7-13$) the most surprising behavior was observed: Filling the trap with CO in addition to O_2 resulted in a partial reduction or even a complete vanishing of $Ag_nO_4^-$ signals and a corresponding increase of the bare Ag_n^- cluster signals for odd n, while the $Ag_nO_2^-$ peaks (n even) and Ag_{13}^- remained unaffected by CO addition. Figure 3 shows the corresponding product ion mass spectra at 100 K and equal reaction times, but under different reaction conditions: (a) When only trace amounts of oxygen are present in the trap, odd size clusters Ag_7^-, Ag_9^-, and Ag_{13}^- do not react, Ag_{11}^- yields some product $Ag_{11}O_4^-$, while even size clusters completely react to $Ag_nO_2^-$ products. (b) When the oxygen partial pressure is raised to 0.01 Pa, Ag_7^- reacts and forms the oxide $Ag_7O_4^-$, Ag_9^- almost completely disappears and the products $Ag_9O_2^-$ and $Ag_9O_4^-$ are observed, also the Ag_{11}^- signal almost vanishes and $Ag_{11}O_4^-$ remains. The product ion mass spectrum (c) was obtained under conditions where partial pressures of both reactants, O_2 and CO, are present in the trap. Unexpectedly, the bare silver cluster

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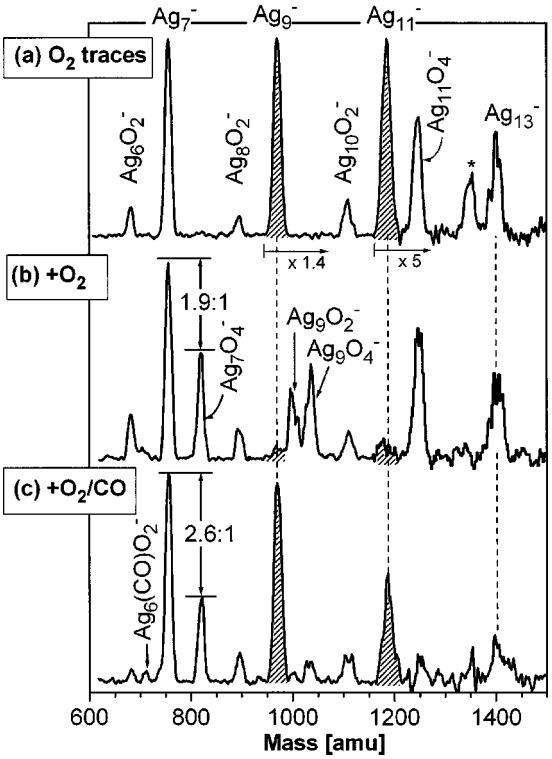

FIG. 3. Product ion mass spectra of silver clusters Ag_{7-13}^- obtained at $T_R = 100$ K and $t_R = 0.1$ s with different reactant concentrations in the ion trap. (a) Reaction with trace amounts of oxygen. $p_{He} = 1.2$ Pa. (b) Reaction with oxygen. $p_{O_2} = 0.01$ Pa, $p_{He} = 1.17$ Pa. (c) Reaction with oxygen and carbon monoxide. $p_{O_2} = 0.01$ Pa, $p_{CO} = 0.03$ Pa, $p_{He} = 1.17$ Pa. In the case of Ag_7^- the bare to oxide cluster signal ratio is indicated in (b) and (c). The Ag_9^- and Ag_{11}^- mass peaks (hatched) disappear almost completely after reaction with oxygen and reappear when CO is added. The peak in (a) labeled by an asterix would correspond to the mass of $Ag_{12}O_4^-$, but is only observed at extremely low oxygen partial pressures (traces) and does not appear at measurable O_2 content.

signals Ag_9^- and Ag_{11}^- reappear, while the corresponding oxide product intensities decrease considerably. Also in the case of Ag_7^-, the bare to oxide cluster ratio shifts in favor of the bare Ag_7^-. This pronounced signal enhancement of the bare metal clusters cannot be explained by fragmentation of larger clusters, because signal intensities are much weaker for the larger cluster sizes (cf. Fig. 3).

Considering the fact that the pure metal clusters do not react with carbon monoxide the conclusion can be drawn that CO reacts with the oxides of Ag_7^-, Ag_9^-, and Ag_{11}^-. The observed complexes $Ag_nO_4^-$ are then the decisive intermediates in the reaction with CO. The potential catalytic activity of $Ag_nO_4^-$ complexes has been indicated in theoretical calculations for the smaller clusters $Ag_3O_4^-$ and $Ag_5O_4^-$ previously.[10] The present data provide evidence that, in contrast to other cluster sizes, silver cluster anions with $n = 7$, 9, and 11 activate the adsorbed oxygen to be able to react with CO under our reaction conditions. In this process CO_2 is likely to be liberated and the metal clusters are reformed to complete a catalytic reaction cycle. Theoretical and experimental work is in progress to determine details of such a possible reaction mechanism.[18]

In conclusion, in an rf-octopole ion trap setup under low pressure multicollision conditions, free atomic silver cluster anions show a pronounced size dependence in their reactivity toward O_2. In contrast, no reaction products with CO could be observed. However, reactions with both, O_2 and CO, indicate the catalytic activity of certain investigated cluster sizes (Ag_7^-, Ag_9^-, and Ag_{11}^-) in the CO combustion reaction with $Ag_nO_4^-$ complexes as decisive reaction intermediates.

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