

## Cooperative Effects in the Activation of Molecular Oxygen by Anionic Silver Clusters

Jan Hagen,<sup>†</sup> Liana D. Socaciu,<sup>†</sup> Jérôme Le Roux,<sup>†</sup> Denisia Popolan,<sup>†</sup> Thorsten M. Bernhardt,<sup>\*,†</sup> Ludger Wöste,<sup>†</sup> Roland Mitrić,<sup>‡</sup> Holger Noack,<sup>‡</sup> and Vlasta Bonačić-Koutecký<sup>‡</sup>

*Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany, and Institut für Chemie, Humboldt Universität zu Berlin, Brook-Taylor-Strasse 2, D-12489 Berlin, Germany*

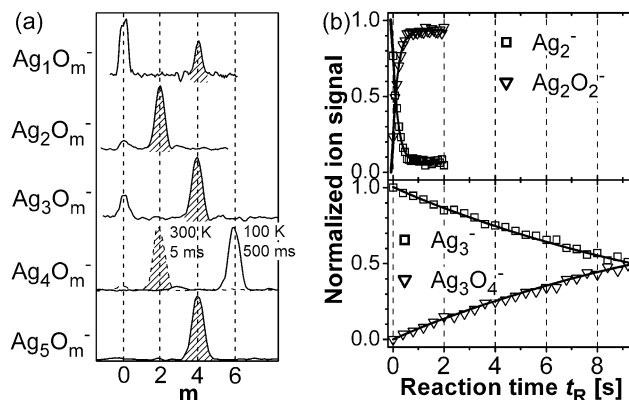
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Supported silver particle catalysts are employed in the important industrial ethylene oxidation processes involving molecular oxygen.<sup>1</sup> Although a great deal of information about the catalytic activity of silver is available, the details of the oxidation reaction mechanism remain elusive. What seems clear is that the rate-determining step involves some form of oxygen bound to the silver particle surface.<sup>1,2</sup> The study of the interaction of silver particles with molecular oxygen therefore aims to add to an understanding of elementary catalytic reaction steps. In this respect, the experimental techniques of modern cluster science provide two major advantages. First, the reaction system, i.e., number of atoms in the cluster and charge state, can be defined exactly in a controlled environment. Second, due to the finite size of clusters, a direct treatment by ab initio theoretical approaches is amenable.

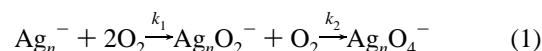
In this communication, we present mass spectra and kinetic measurements that reveal an unprecedented size dependence in the adsorption of multiple oxygen molecules onto anionic silver clusters  $\text{Ag}_n^-$  ( $n = 1-5$ ). Theoretical results obtained employing DFT method completely reproduce the observations and provide a mechanism based on cooperative electronic effects responsible for size selective reactivity of anionic silver clusters toward one or more oxygen molecules. In particular, we show that one weakly bound  $\text{O}_2$  provokes the reactivity of closed shell clusters  $\text{Ag}_n^-$  (odd  $n$ ) toward a second  $\text{O}_2$  molecule, which is then in turn strongly bound in an activated superoxo-like state.

The gas-phase ion beam apparatus employed in the present investigation allows the storage of free mass-selected cluster ions in a radio frequency (rf)-octopole ion trap for a defined time of a few milliseconds up to seconds without significant loss in ion intensity.<sup>3</sup> The trap is filled with about 1 Pa of helium buffer gas and a small partial pressure of molecular oxygen. Temperature control inside the ion trap (20–300 K) is achieved via a helium cryostat attached to the trap enclosure. The storage time of the ions defines the reaction time  $t_R$  after which all product ions are extracted and mass analyzed. The recorded product ion concentrations as a function of  $t_R$  are finally fitted by the integrated rate equations of the proposed reaction mechanism to yield the rate constants.

Product ion mass spectra measured after reaction of mass-selected silver clusters with oxygen are depicted in Figure 1a. An alternating size dependence in the reaction behavior is observed. Silver clusters with odd number  $n$  of silver atoms adsorb at maximum two oxygen molecules, whereas  $\text{Ag}_n^-$  with even  $n$  adsorb only one  $\text{O}_2$ . However,  $\text{Ag}_4^-$  first forms  $\text{Ag}_4\text{O}_2^-$ , but then reacts with additional two  $\text{O}_2$  at long reaction time and low temperature (cf. Figure 1a). No products with an odd number of oxygen atoms are detected. The corresponding kinetic data (cf. Figure 1b) are best fitted by a sequential adsorption reaction mechanism:



**Figure 1.** (a) Product ion mass spectra after reaction of  $\text{Ag}_n^-$  with  $\text{O}_2$ . Ion intensities are plotted as a function of the number of adsorbed oxygen atoms  $m$ . Conditions are chosen to achieve comparable product ion intensities for different cluster sizes:  $T_R = 100$  K in all cases, except for  $\text{Ag}_2^-$  and for  $\text{Ag}_4^-$  (dashed line), where  $T_R = 300$  K. (b) Examples of measured oxidation kinetics for  $\text{Ag}_2^-$  and  $\text{Ag}_3^-$  at 300 K. Open symbols: experimental data; solid lines: kinetic fit.  $\text{Ag}_2^-$ :  $p_{\text{O}_2} = 0.12$  Pa,  $p_{\text{He}} = 1.06$  Pa.  $\text{Ag}_3^-$ :  $p_{\text{O}_2} = 0.23$  Pa,  $p_{\text{He}} = 1.03$  Pa.



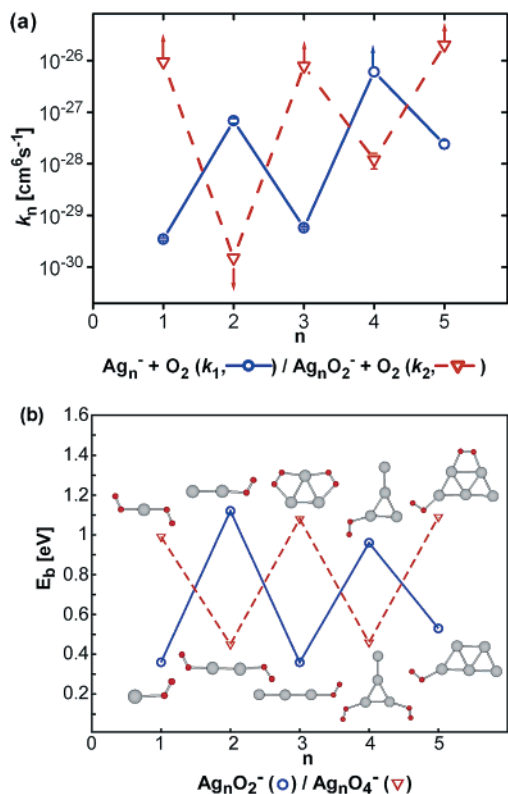
The fit of the integrated rate equations is represented by the solid lines in Figure 1b. The rate constants  $k_1$  and  $k_2$  at 300 K are plotted in Figure 2a as a function of cluster size. Note that the rates change over at least 2 orders of magnitude when the size of the clusters is increased by a single atom. Rate constants  $k_1$  for the silver cluster reactions with  $\text{O}_2$  have been reported before,<sup>4</sup> and these results are in reasonable agreement with our data. However, in the previous report, products with more than one  $\text{O}_2$  have not been observed for  $\text{Ag}_n^-$  ( $n = 1-5$ ).

The obtained rate constants are termolecular under the low-pressure multicollision conditions of the experiment (Lindemann model for gas-phase association reactions).<sup>5</sup> They include the elementary steps of the initial formation of an energized complex (rate constant  $k_a$ ) and its possible unimolecular decomposition back to the educts ( $k_d$ ) in competition with a stabilizing energy transfer collision with helium buffer gas ( $k_s$ ).<sup>5</sup> As the ion–molecule reaction rate constants  $k_a$  ( $\sim 5.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ) and  $k_s$  ( $\sim 5.3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ) show no significant cluster size dependence,<sup>6</sup> the observed strong size effects must be contained in  $k_d$  (see below).

For  $\text{Ag}_n^-$  ( $n = 1, 3, 5$ ) the sequential adsorption of two oxygen molecules on the odd size clusters takes place without appearance of intermediate products  $\text{Ag}_n\text{O}_2^-$  in the product ion mass spectra. This points toward the adsorption of the first  $\text{O}_2$  being the rate-determining step, whereas addition of the secondary  $\text{O}_2$  must proceed on a much faster time scale than the resolution of our experiment ( $k_d < 10^7 \text{ s}^{-1}$ ). Lower limits for  $k_2$  are given in these

<sup>†</sup> Freie Universität Berlin.

<sup>‡</sup> Humboldt Universität zu Berlin.



**Figure 2.** (a) Experimental rate constants obtained for the adsorption of the first and second  $\text{O}_2$  molecule onto  $\text{Ag}_n^-$  at  $T_R = 300$  K. (b) Theoretical binding energies  $E_b$  and lowest energy structures (gray spheres: silver atoms; red spheres: oxygen atoms). Note that the lowest energy structures of  $\text{Ag}_2\text{O}_2^-$  and  $\text{Ag}_3\text{O}_4^-$  contain dissociated oxygen (not shown), which requires considerable activation energy not available under our experimental conditions.

cases in Figure 2a. On the other hand, the adsorption of a second  $\text{O}_2$  onto  $\text{Ag}_2^-$  is not observed in the experiment, and therefore an upper limit for the corresponding  $k_2$  value is estimated.

To explain our experimental results, and in particular to account for the multiple adsorption of molecular oxygen onto the anionic clusters with odd number of atoms, we perform a systematic theoretical study in the framework of density functional theory. We use Becke's hybrid three parameter nonlocal exchange functional combined with the Perdew–Wang correlation functional (B3PW91).<sup>7</sup> For silver, a 19-electron relativistic effective core potential (19e-RECP) from the Stuttgart group and [8s7p6d1f/6s5p3d1f] AO basis set have been employed.<sup>7,8</sup> The applied methodology allows us to accurately determine structural properties and binding energies, especially when the bonding with oxygen is involved.<sup>8</sup> The experimentally obtained reaction rate constants (Figure 2a) compare particularly well with the trend in the calculated  $\text{O}_2$  binding energies  $E_b$  (Figure 2b) because, according to statistical rate theory,<sup>5</sup>  $E_b$  largely determines the rate of unimolecular decomposition of the initially formed energized complex ( $k_d$ ; cf. above discussion).

The results can be assessed by qualitative considerations for the binding of molecular oxygen to anionic silver or gold clusters based on the frontier orbital model.<sup>4,8,9</sup> The oxygen molecule, as a one-electron acceptor, binds strongly to the anionic silver clusters with odd number of electrons (even  $n$ ) and low vertical detachment energy (VDE) values, leading to a small  $k_d$  and, hence, to a fast reaction rate  $k_1$ . In contrast, it binds only weakly to silver clusters with even number of electrons (odd  $n$ ) and closed shell electronic structure, resulting in low reaction rates  $k_1$  in these cases. However,

recent work on reactivity of hydrated anionic gold clusters with molecular oxygen has shown that this behavior can be inverted by binding of a strong electron acceptor such as the OH group.<sup>8</sup> Due to the electron withdrawing effect, electron transfer from the cluster occurs leaving an unpaired electron on the clusters with even number of electrons and inducing subsequent stronger binding of the molecular oxygen to hydrated clusters. We propose an analogous mechanism for the activation of molecular oxygen and the cooperative binding of two oxygen molecules on the anionic silver clusters in which the first adsorbed  $\text{O}_2$  serves as an activator. Since anionic silver clusters have generally lower VDE values than gold clusters, weaker electron acceptors such as  $\text{O}_2$  can already induce electron transfer and activate them. The first oxygen molecule is bound to the silver clusters with even number of electrons by 0.36, 0.36, and 0.53 eV for  $\text{Ag}^-$ ,  $\text{Ag}_3^-$ , and  $\text{Ag}_5^-$ , respectively. The mechanism of the bonding involves the electron transfer from the metal cluster into the  $\pi^*$ -MO of  $\text{O}_2$ . The binding of the first  $\text{O}_2$  molecule changes the electronic structure of the cluster and induces a stronger cooperative binding with the second  $\text{O}_2$ . This results in the case of  $\text{Ag}_3^-$  and  $\text{Ag}_5^-$  in new oxide species with doubly bound, superoxo-like  $\text{O}_2$  subunits, as can be seen from the calculated structures in Figure 2b. The cooperative effect is reflected in larger binding energies as shown in Figure 2b. In fact, due to the fast binding of the second  $\text{O}_2$ , the complexes with only one  $\text{O}_2$  have not been observed for  $\text{Ag}^-$ ,  $\text{Ag}_3^-$ , and  $\text{Ag}_5^-$ . Moreover, the binding of the second molecular oxygen shows a reversed pattern being stronger for clusters with an odd number of atoms and weaker for the ones with an even number of atoms. The latter ones with one unpaired electron bind strongly only one oxygen molecule since the electron transfer leaves them with a closed shell electronic structure. The above mechanism can be extended to the absorption of three oxygen molecules which should qualitatively exhibit the similar behavior as the adsorption of one  $\text{O}_2$ . Adsorption of three  $\text{O}_2$  molecules has indeed been detected experimentally for  $\text{Ag}_4^-$  (cf. Figure 1a).

In conclusion, our joint experimental and theoretical work shows pronounced size and structure selective activity of anionic silver clusters toward molecular oxygen due to cooperative effects. In particular, for  $\text{Ag}_n^-$  clusters with odd  $n$  a weakly bound first  $\text{O}_2$  promotes the adsorption of a second  $\text{O}_2$  molecule, which is then (for  $n = 3, 5$ ) differently bound with the  $\text{O}_2$  bond elongated to 1.32 Å and thus activated for further oxidation reactions such as CO combustion. These findings of coadsorption properties on  $\text{Ag}_n^-$  clusters are conceptually important for the understanding of the role of silver clusters in oxidation processes. Further theoretical and experimental work on this subject is in progress.

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