Oxygen and Silver Clusters: Transition from Chemisorption to Oxidation

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We use the adsorption probabilities of molecular nitrogen and oxygen to study the physi- and chemisorption on small silver particles. The physisorption of nitrogen is governed by the structure of the particle surface. The sticking of oxygen additionally involves the electronic configuration of the metal cluster. At 77 K molecular oxygen sticks chemisorbed to the particles with a transfer of one electron. At temperatures above 105 K the chemisorption transforms into oxidation, invoking the dissociation of the oxygen molecule and the loss of a single oxygen atom.

The interaction of oxygen with metal has already motivated a large number of intensive studies for more than a century, both on fundamental and industrial aspects. Among these investigations, the silver metal has attracted a particular attention with respect to its fascinating charge transfer behavior in diverse domains like its peculiar bactericidal properties [1], its large fluorescence enhancement [2], and its fundamental catalytic role in the epoxidation of ethylene [3].

For oxygen-silver surface interaction, the mechanism generally accepted is characterized by the physisorption of O_2 at low temperature, followed on warming by a molecularly chemisorbed state, explained by an electron transfer from the metal to the O_2 antibonding π^* orbital that is the precursor state for its dissociation [4]. Additional heating transfers this superoxide O_2^- to the peroxide molecule O_2^{2-}, which is instable and dissociates [5,6]. It has been reported for more reactive surfaces such as Cs [7] and Al [8] that one of the atoms can be ejected while the other gets trapped on the surface. Finally, but only at high oxygen pressure, a lattice restructuration occurs and silver oxide is formed, in which the O reaches the oxidation state of -2 [4].

With the recent increasing use of nanomaterials, understanding the oxidation of nanometer scale materials is of considerable importance. However, up to now, little attention has been paid to the oxidation of nanoparticles. Considering clusters as precursors of nano-objects, the fundamental question concerns the extent to which gas phase nanoclusters can exhibit catalytic activity, and serve as a prototype of coupling oxygen with a finite reservoir of electrons.

There are few experimental attempts concerning the reaction of O_2 with noble metal clusters and molecules [9–13]. By using a flow tube reactor it was observed that only O_2 sticks on clusters. In no case have odd-numbered oxidized products been detected. Moreover, in the case of adsorption of O_2 on cluster anions, it was concluded that O_2 acts as a single-electron acceptor yielding adsorbed superoxide O_2^-, as at the bulk surface [12,14]. By contrast, when cold, neutral silver clusters are formed in an oxygen atmosphere and strongly heated by a laser ionization and excitation, Ag_nO_m has been found with no preference to odd numbers of n. It has been shown that in this case the oxygen atom is bond to two silver atoms to form an Ag_2O molecule in the silver cluster [15].

In this Letter we demonstrate the link between these two behaviors by performing an experiment on silver nanoclusters cations in interaction with oxygen at variable temperature. We show evidence of a temperature-induced transition from the molecular chemisorbed O_2^- to silver oxidation, where two charges are localized on silver atoms to form an Ag_2O molecule. By contrast to the silver bulk the other O atoms is ejected, when the O_2^- dissociates. We demonstrate that this process is cluster size dependent and implies both its shape and its electronic structure. Moreover, it occurs for small sizes at temperatures less than 110 K.

The experimental procedure is briefly the following: After production of pure, silver cations at 77 K, oxygen or alternatively less reactive gas as nitrogen is injected into the source chamber. Cluster and gases pass through a thermalization and reaction chamber with variable temperature [16]. The reaction products and their temperature dependence are studied by a reflectron time of flight mass spectrometer [17] (Fig. 1).

The cold silver cluster cations are produced by using a gas aggregation source at 4–100 mbar He pressure in a liquid nitrogen cooled (77 K) aggregation chamber. A
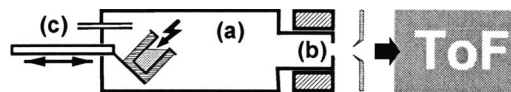

FIG. 1. The schematic experimental setup. See text for description. The aggregation chamber (a) is liquid nitrogen (77 K) cooled. A thermalization and reaction chamber (b) serves as a heat bath with variable temperature. The hatched elements are electric heaters. The entrance for buffer and reaction gas is indicated by (c).

discharge in between the vaporizer oven and aggregation chamber ionizes the clusters. The missing magic numbers in the mass spectrum of the pure silver [Fig. 2(a)] indicates that no fragmentation occurs during the cold growing and ionization process [18].

After the injection of O_2 or N_2 at 77 K into the source chamber, the depletion of certain Ag_n^+ is observed and accompanied by the appearance of the corresponding $Ag_nO_2^+$ or $Ag_n(N_2)_m^+$ at 32 amu or 28, respectively [Figs. 2(b) and 2(c)].

By injecting first N_2, which is expected to be only physisorbed on clusters [19], we found that the number of attached nitrogen molecules increases with the N_2 pressure up to characteristic saturation values. Heating the particles compensates this increase. The process is therefore an equilibrium of sticking and evaporation of N_2 on each Ag_n^+. Above 110 K all nitrogen desorbs in the size range shown in Fig. 2 in agreement with a weak, induced dipole-dipole interaction. The adsorption proba-

bilities vary due to the surface structure of the particle. Surface atoms with low coordination numbers stronger physisorb the molecules [20]. For this reason small clusters strongly attract the nitrogen and differences in the cluster geometrical structure generate pronounced cluster size dependent variations as shown in Fig. 3(a).

By injecting oxygen instead of nitrogen it sticks to the clusters at 77 K with some similarities and differences to nitrogen. By contrast to nitrogen, the adsorption probability of O_2 generally increases with cluster size. Furthermore it is less sensitive to the pressure. The first $Ag_nO_2^+$ appears like the first $Ag_nN_2^+$ at gas pressures below 5×10^{-5} mbar. At 10^{-2} mbar several nitrogen molecules stick to all the studied clusters sizes up to 27 silver atoms, but only to Ag_n^+ with $n \in \{22, 23, 24\}$ more than one single O_2 could be attached at the same O_2 pressure.

Particle sizes, which are less attractive to nitrogen (e.g., 11 and 14 in Fig. 2), are the same to oxygen. This indicates that also for oxygen the cluster shape is relevant for the adsorption probabilities. Nevertheless, superposed to this general trend a strong odd-even alternation is present in the O_2 sticking probabilities [Fig. 3(b)].
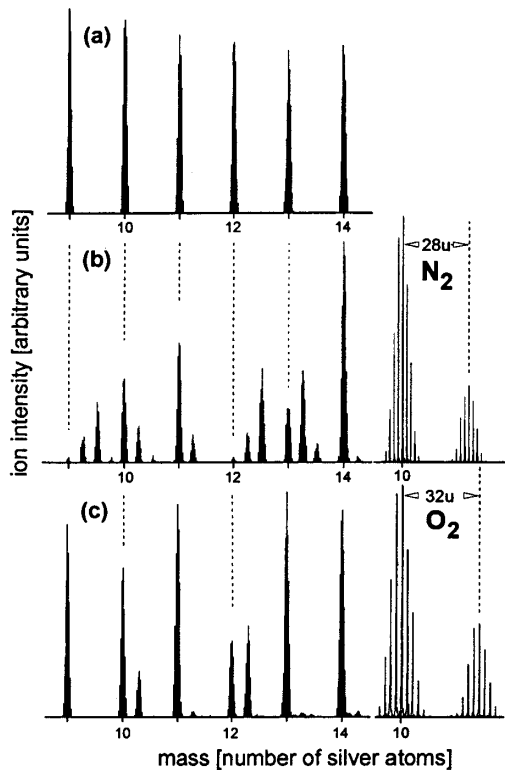

FIG. 2. Mass spectra of positively charged silver clusters at 77 K. (a): pure silver Ag_n^+. (b,c): After interaction with 10^{-4} mbar N_2 (b) or O_2 (c). The molecules stick to the cold clusters with characteristic size dependent preferences. The right part of the mass spectra shows expanded the isotopic distribution of silver. The peaks of $Ag_{10}N_2^+$ and $Ag_{10}O_2^+$ are shifted by 4 atomic units and are clearly separated by the spectrometer. Beside preferences due to the particle surface geometry, visible for N_2 and O_2, oxygen prefers sticking to clusters with an unpaired electron in their finite electron reservoir (see Fig. 3).
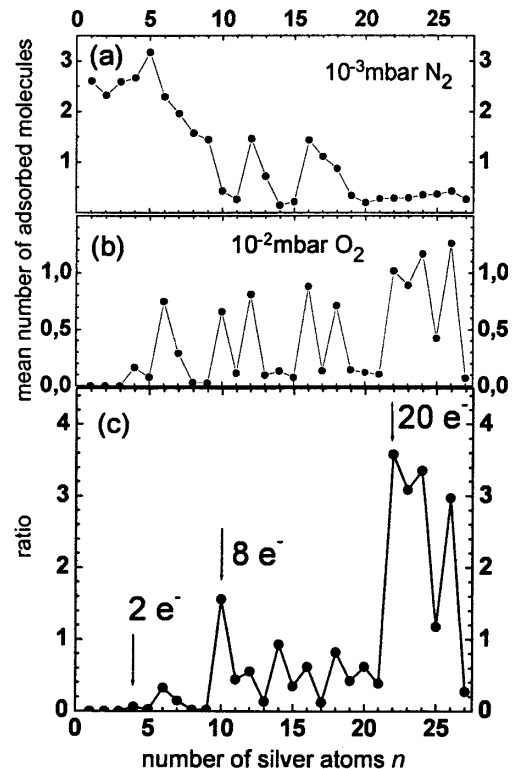

FIG. 3. The mean number of N_2 $\langle_{N_2}(n)\rangle$ and (b) of O_2 $\langle_{O_2}(n)\rangle$ adsorbed to the cluster of size n at given pressure. (c): The ratio $\langle_{O_2}(n)\rangle/\langle_{N_2}(n)\rangle$ removes the influence of the surface geometry. The remaining pattern shows the characteristic odd-even alternations and shell closings of an electronic influence for the O_2 interaction. One electron is transferred from the cluster to the chemisorbed O_2^-.

In order to fix these differences Fig. 3 shows the ratio $\langle_{O_2}(n)\rangle/\langle_{N_2}(n)\rangle$, where $\langle_X(n)\rangle$ is of the mean number of $X = O_2, N_2$ sticking to the cluster of size n. The pressures in (a) and (b) have been chosen to be below saturation but high enough to avoid zero adsorption probabilities. Figure 3(c) shows the characteristic odd-even alternation of paired and unpaired electrons and steps at 10 and 22 silver atoms, which correspond to the well-known 8 and 20 electron shell closing of the free electrons in the small metal particle [15]. Obviously there is a preference in sticking of O_2, if the pure, positively charged cluster has an *unpaired* electron and it works best, if there is *one* electron too much for a shell closing.

Therefore we conclude that this, for the particle redundant, electron is transferred to the oxygen molecule. The chemisorption is more stable if it optimizes the electronic configuration of the electron reservoir in the metal particle [Fig. 4]. This molecular chemisorption with a transfer of one e^- from the metallic cluster to the oxygen is similar to the one already observed for bulk silver surfaces [4] and for anionic noble metal clusters [12].

By contrast to the bulk the electron reservoir of the cluster is *finite*. A chemisorption therefore charges the cluster additionally by one elementary charge. Since the number of e^- that can be extracted out of the small reservoir is limited, a chemisorbed molecule protects the cluster against further chemisorption. This explains why more than one chemisorbed oxygen has only been found for clusters with a size above 22 atoms and why it is in general more difficult to chemisorb O_2 at smaller sizes.

In a last experimental step the reaction chamber was heated. As mentioned before the physisorbed nitrogen molecules can easily be desorbed by this procedure and the pure silver spectrum appears again. Applying the same procedure to silver clusters with chemisorbed molecular oxygen leads to a different result. Above 105 K silver clusters with *single* oxygen atoms appear in the expanded spectra as shown in Fig. 5. This indicates that the silver has dissociated the O_2 and that one O atom is directly ejected during the dissociation.

Subsequent laser heating of the $Ag_n{}^+O$ products shows evidence of the evaporation of Ag or Ag_2 and reveals the electronic structure of the metallic silver core. It shows up that the oxygen atom is bond in Ag_2O oxide molecule giving $Ag_{n-2}{}^+Ag_2O$ [15]. Figure 5 shows that $Ag_n{}^+O$ also appears when $Ag_n{}^+O_2$ does not exist in the mass spectrum at low temperature. Two reasons may be invoked: First the reaction enthalpy of the oxidation could be sufficient to evaporate Ag or Ag_2. This could explain the appearance of Ag_9O^+ even without $Ag_9{}^{++}O_2{}^-$ either from $Ag_{10}{}^{++}O_2{}^-$ or from $Ag_{11}{}^{++}O_2^-$. Second, the appearance of Ag_9O^+ without the chemisorbed O_2^- could indicate that clusters with paired electron configurations drop directly into the oxidized states without being trapped chemisorbed. Compared to the unpaired situation it needs a higher temperature to pass the barrier into the
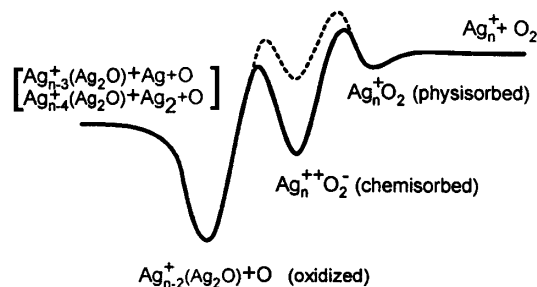

FIG. 4. Schematic energy potential diagram for the interaction of oxygen and silver: Beside the oxidized state, which was studied earlier [15], the *molecular chemisorbed* state has been found for small clusters. Here *one* electron is transferred form the particle to the O_2 molecule. Depth and barrier height of this state varies with the electronic configuration of the cluster (dotted line). The *physisorbed* state of oxygen cannot be observed directly at 77 K, but on particles with a strong physisorption O_2 easier enters the chemisorbed state.

chemisorbed states but a lower one to oxidize the chemisorbed cluster (see solid and dotted line in Fig. 4). Since both temperatures are close anyway, the intermediate, chemisorbed state might be no longer populated for some clusters with paired electronic configuration. The chemisorption is then just a transition state.

In summary, we have shown that the interaction of small silver clusters and oxygen has three separable stages. At lowest temperatures the oxygen molecule is
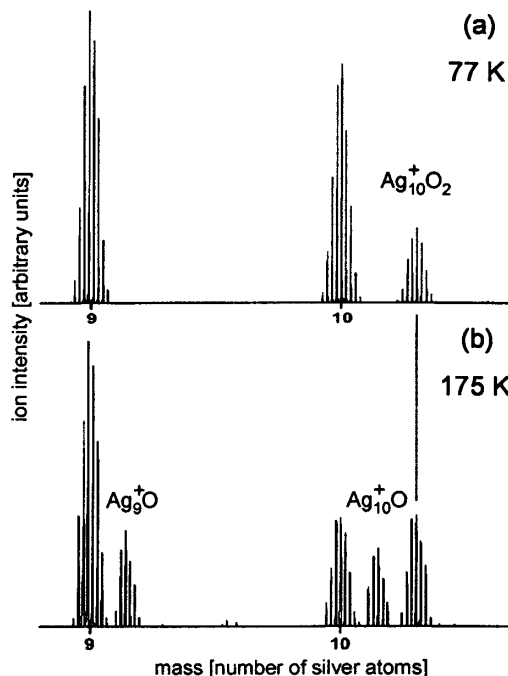

FIG. 5. Mass spectra of silver clusters grown at 77 K in the presence of oxygen. By contrast to (a) in (b) the clusters are heated after the production in a separate chamber to 175 K. The appearance of single oxygen atoms indicates the dissociation of the O_2 molecules.

physisorbed. As for the nitrogen the strength of the physisorption reflects the cluster shape. At a temperature less equal 77 K the oxygen molecule takes one electron from the delocalized valence electrons of the particle and reaches the chemisorbed state. The chemisorption is favored if the loss of one electron optimizes the free electron configuration in the metal particle, showing evidence that the remaining charge is delocalized in the silver cluster. Hence, the number of chemisorbed molecules is limited by the number of electrons that can be extracted out of the small silver particle.

Finally, at temperatures above 105 K the chemisorption transforms into oxidation, in which the O reaches the oxidation state of -2. This involves the dissociation of the oxygen molecule and, by contrast to bulk silver, an ejection of a single, highly reactive oxygen atom. The remaining metallic part can undergo a new cycle of chemisorption and oxidation allowing the complete cluster to oxidize.

The small energy barrier between chemisorption and oxidation, which is overcome at 105 K, indicates that the O-O bond in the chemisorbed O_2 at the silver cluster is weaker than at a bulk surface. This should positively influence the oxidizing catalytic activity of the silver nanoparticles. As a consequence gas phase silver cluster serve as a vehicle for this strongly activated oxygen.

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