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ARTICLE

Adsorption of O₂ on Anionic Silver Clusters: Spins and Electron Binding Energies Dominate in the Range up to Nano Sizes

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Exploring the reactivity of metal clusters is an important task in cluster science, while only a few previous studies involve the reactions of nano-sized ones. Here we report a kinetic measurement on reactions of Ag_n⁻ (n = 6 - 69) with O₂ using a flow reactor running at 120K. Their relative rates were obtained by fitting decay processes of parent ions at different O₂ flows. Comparing the variations of the kinetic rates and the photodetachment energies of Ag_n⁻ (i.e. the binding energies of their excess electrons), we distinguished the separate effect of clusters' spins or their electron binding strength. This work firstly shows that reactions of O₂ and Ag_n⁻ up to nano sizes are still dominated by clusters' global electronic properties. This conclusion is conceptually important for understanding the reaction mechanisms on silver based nano catalysts.

1. Introduction

Silver based catalysts are widely used in producing ethylene epoxide from ethene and methanal from methanol in chemical industry.¹ They also play an important role in oxidation of soot in exhausts.² In order to understand the mechanisms of these catalytic reactions, various model systems have been applied to simulate the active sites on these heterogeneous catalysts. Metal clusters in gas phase are ideal models for this purpose.³⁻¹² Interaction of O₂ with many Ag_n⁺ were reported,¹³⁻¹⁵ while lack of knowledge on electronic properties of cluster cations make it difficult to carry on in-depth explorations. The anionic silver clusters attract more attentions because their electronic structures have been acquired by photoelectron spectroscopy experiments,^{16, 17} and additionally the excess negative charges in anionic clusters are helpful to activate O₂ molecule.^{5, 18-25} The rate constants for the reactions of Ag_n⁻ (n=1-13) with O₂ have been measured at room temperature, which show an evident even odd oscillation.²⁶ The fast reactions of even sized clusters (with odd number of electrons) were attributed to two factors: the easy electron transfer from these clusters to π* of O₂ due to their low electron binding energies, and the attractive electron pairing tendency between the single electrons on the clusters and O₂. Bernhardt and co-workers studied the interaction of O₂ with Ag_n⁻ (n = 1-11) at 100-300 K and deduced the binding energies of O₂ on Ag_n⁻ (n = 1-5).^{22, 23, 27} The binding strengths on Ag_n⁻ (even n) are apparently stronger than those of the odd sized ones. This trend was well interpreted using the electron transfer model.

Castleman and co-workers studied adsorptions of O₂ on Ag_n⁻ (n = 11 - 20) at room temperature and discussed the importance of spin accommodation.^{28, 29} Their conclusion is that a spin crossing is involved in these reactions and spin excitation is needed for Ag_n⁻ (odd n) when they interact with O₂. Therefore, the energies needed for the excitation processes determine clusters' reactivity. Theoretical works reproduced the even odd oscillation of O₂ binding energies on Ag_n⁻, which is inverse to the trend of their electron binding energies.^{22, 23, 27} At the same time, calculations also provide evidences for the spin effect. For example, the theoretical HOMO-LUMO gap of Ag₁₃⁻ is large, which endows this cluster with a large spin excitation energy and therefore enhanced stability.²⁸ For Ag_n⁻ with n = 1-20, the sizes with an unpaired electron always have relatively low electron binding energies.^{16, 17} Thus, the effects of spins and electron binding energies are always to the same direction, and hence have not been separately distinguished.

In addition to small silver clusters in gas phase, many larger model systems were synthesized and characterized in condensed phases. These systems include mono disperse silver particles ranging from nano to micro meters.³⁰⁻³⁴ The reactions of O₂ with these large particles are affected by many complicated factors, including particles' electronic properties such as the band gaps, the structural details around the adsorption sites, and additionally the components and structures of the supporting substrates. For these systems, that is quite difficult to distinguish the effects of clusters' intrinsic properties and those of their surroundings. Clusters around 1 nm play very important roles in many catalyst systems,^{35, 36} while there are even more challenges to prepare and characterize these sizes than the large nano particles. The reactivity of silver clusters with defined sizes around 1 nm was rarely involved by previous studies in condensed phases.

In the current article, we use a flow reactor to study O₂ adsorption on Ag_n⁻ (n = 6 - 69) in gas phase. The Ag₅₅⁻ has an

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icosahedron structure,^{37, 38} and its dimension is estimated to be around 1 nm. Therefore, the cluster sizes in this work cover the range from very small silver clusters to those with dimensions around 1 nm. The comparisons between the trends of their kinetic rates and electron binding energies provide separate evidences for the two fundamental mechanisms, spin accommodation and electron transfer. More importantly, this study shows that Ag_n^- around 1 nm perform very similar to the small sized ones in the reactions with O_2 , i.e. global electronic properties rather than local structural details dominate.

2. Experimental methods

The anionic silver clusters were generated by a magnetron sputtering cluster source,³⁹ which was previously used on a TIED instrument.^{40, 41} The scheme of this source was shown in Fig. 1, including a liquid nitrogen cooled aggregation chamber enclosing a magnetron sputter discharge head. In this work, the helium flow and the argon flow was kept at 110 sccm and 14 sccm, respectively. The constant liquid nitrogen (LN_2) flow cooled the chamber to about 105 K and the pressure inside the aggregation chamber was about 0.5 torr. A tube reactor was installed at the exit of the source chamber, the details of which were shown in the insert of Fig. 1. All components of this reactor are made of copper and isolated from the aggregation chamber using a ceramic spacer. Its temperature can be stabilized at a set point using a controlled heater, which was 120 ± 1 K in this study. All clusters entered the reactor with gas flow and firstly experienced a thermalization region, where buffer gases were thermalized by compact copper meshes. For cluster species, the collisions with gas molecules in this region were up to thousands of times, which ensured the cluster temperature being heated to the set point. Then, all clusters entered the reaction area where 0-4 sccm O_2 were introduced through two copper tubes extending close to the axial center of the reactor. The parent or product clusters were sampled by a skimmer at the end of the reactor and were direct to a Time-of-flight mass spectrometer running at about 800 Hz.

In this work, the total pressure in the reactor was a few tenths of torr and the reactions were in the kinetic low-pressure regime of the Lindemann-type mechanism. When the adsorption reactions are understood based on this mechanism as in many previous works,^{23, 26, 42-44} a termolecular rate constant k_{III} can be used to represent a cluster's reactivity. For the present measurements, it is hard to precisely estimate the parameters of the total gas pressure, the O_2 concentration and the retention time of cluster anions in the reactor, which makes it impossible to directly obtained the kinetic rates k_{III} . However, the cluster source and the reactor run in continuous mode, and the gas parameters at each point were constant during measurements. The O_2 concentrations in the reaction region could vary with positions, while the value at each point should be in proportion to the O_2 flow rates. Then, the $-\ln(I/I_0)$ should have a linear relationship with the O_2 flow rate, in which the I and I_0 stand for the parent ion intensities at certain O_2 flow rate and that without O_2 at all, respectively. The relative rate of each size

is represented by the slope in linear fitting of $-\ln(I/I_0)$ vs O_2 flows, and the termolecular rate constant k_{III} is in proportion to this fitting slope. The factor for this proportionality was calibrated using the reaction of Au_2^- with O_2 under the same condition, in which the k_{III} value was estimated from a previous measurement using a cold trap.²³ The data of the reactions of Au_2^- and O_2 is shown in Fig. SP as a supporting material. Because the ratio of argon insider the reactor is only about 11% and the collision rate constants of an ion with argon and helium are very close,⁴⁵ the difference between argon and helium is neglected in estimating k_{III} .

3. Results and discussion

3.1 Molecular adsorption of O_2

Fig. 2 a-c show the mass spectra of Ag_n^- ($n = 6-39$) with O_2 flow rates of 0.000 sccm, 0.035 sccm and 0.213 sccm, respectively. Fig. 2 a'-c' show the mass spectra of Ag_n^- ($n = 40-81$) under the same conditions. Because silver has two isotopes with nearly equal abundances (51.8% for 107 Da and 48.2% for 109 Da), the peaks in mass spectra become broad with increasing cluster sizes. The signals for Ag_n^- and Ag_nO_2^- can be well resolved with $n \leq 50$, and can roughly be separated using peak profile simulations in size range of $51 \leq n \leq 60$. For cluster of Ag_n^- ($61 \leq n \leq 69$), we can still distinguish whether Ag_nO_2^- were generated or not, while the signals for Ag_n^- and Ag_nO_2^- become completely unsolved for $n \geq 70$. In Fig. 2a and a', nearly all peaks correspond to clean Ag_n^- . In Fig. 2 b, c, b' and c', the products Ag_nO_2^- are labeled using empty circle symbols and the Ag_nO_4^- are labeled using solid ones. In the size range of $n = 6 - 39$ shown in Fig. 2 b and c, nearly all even sized Ag_n^- adsorb one O_2 , except the only inert size of $n = 32$. In addition, some odd sized Ag_n^- with $n = 11, 27$ and 31 can also adsorb O_2 , but their adsorption processes are slower than their even sized neighbors. The sizes with $n = 12, 26, 27$ and 31 can adsorb a second O_2 at high O_2 flow rates. In the size range of $n = 40 - 69$ shown in Fig. 2 b' and c', most of even sized Ag_n^- are active except $n = 46, 54, 56$ and 58 . Two sizes of $n = 43$ and 53 can adsorb a second O_2 molecule at high O_2 flow rates. In the whole considered size range, the active even sized Ag_n^- are indicated using dot lines, and the inert Ag_n^- (even n), including $n = 32, 46, 54, 56$ and 58 , are indicated using dash lines. We can see the Ag_n^- with odd n are generally inert or have relatively low reactivity. We also notice that the total intensity of each parent size Ag_n^- and its products $\text{Ag}_n\text{O}_{2,4}^-$ is nearly constant when O_2 flows is varied. This implies that reaction channels other than molecular adsorptions can be neglected under present conditions. A previous study showed that reactions of Ag_n^- ($n = 11-20$) with O_2 at room temperature have channels of multi O_2 adsorption, O-O bond break and oxygen etching processes.²⁸ These reactions contain tandem steps, some of which have energies barriers. The present work and other measurements using cold trap^{22, 23, 27} indicated that molecule adsorptions dominate at mild conditions (low temperature and low O_2 concentration). It was reported that the first O_2 adsorption on Ag_n^- ($n = 2$ and 4) are fast, while the kinetic rates decrease by more than one order of magnitude for their second O_2 adsorption and the first one on Ag_n^- ($n = 1, 3, 5$).²⁷ The results in Fig. 2 generally show a consistent

oscillation trend in very broad size range. A surprising cooperative effect was reported for O₂ adsorption on Ag_n⁻ (n = 1, 3, 5). The first O₂ on Ag_n⁻ (odd n) withdraws an electron from silver cluster and leaves an unpaired one, which accelerates the second O₂ adsorption by several orders of magnitude.²⁷ In Fig. 2c and c', the sizes with n = 12, 26, 27, 31, 43 and 53 can adsorb two O₂ at high O₂ flow rates. The double O₂ adsorption on the odd sizes with n = 27, 31, 43 and 53 could relate to the aforementioned cooperative effect, but apparently, this effect on large silver clusters is not as significant as that on the small sizes.

3.2 Fitting the kinetic rates

For each Ag_n⁻ with n ≤ 60, the parent ion intensity at certain O₂ flow rate (I) and that without O₂ (I₀) were integrated and normalized. The slope in linear fitting of -ln(I/I₀) vs O₂ flow rate stands for the relative rate of the adsorption process. As examples, the fitting results of four Ag_n⁻ with n = 10, 20, 34 and 49 were shown in Fig. 3. The slopes for all Ag_n⁻ were scaled relative to that of Ag₁₀⁻. For Ag_n⁻ with n = 61 - 69, the high limits of their relative rates were estimated by comparing their decay processes with certain small sizes. The relative rates for all Ag_n⁻ (n = 6-69) were summarized in Fig. 4a, demonstrating their size dependent reactivity. In the kinetic low-pressure regime of the Lindemann-type mechanism, the reaction rate of certain size is independent on the concentrations of O₂, the total pressure of buffer gas and the corresponding rate constant k_{III}. Since the O₂ concentration and the pressure of buffer gases are same for all cluster sizes, the relative rates shown in Fig. 4a are in proportion to their k_{III}. According to the fitting slopes shown in Fig. 3 and the fitting slope and k_{III} value of Au₂⁻ with O₂ in the supporting material, the k_{III} for Ag₁₀⁻ was calibrated to be around 6 × 10⁻²⁶ cm⁶s⁻¹. This value and the low limit for the measurements (~2 × 10⁻²⁷ cm⁶s⁻¹) are indicated in Fig. 4a.

3.3 The Effect of spins extends to nano sizes

In order to understand the origins of the rate variations in Fig. 4a, we plotted the electron binding energies of Ag_n⁻ (i.e. photodetachment energies) from ref[16] and ref[17] in Fig. 4b. For Ag_n⁻ (n ≤ 20), these energies have an evident even-odd oscillation. The Ag_n⁻ (even n) have unpaired electrons and relatively low binding energies. According to either electron transfer model or spin accommodation mechanism, these clusters are more active than the odd sized ones, which were shown in previous studies^{22, 23, 27, 28} as well as the Fig. 4a in this work. In Fig. 4b, the oscillation trend of the electron binding energies disappears for Ag_n⁻ (n > 20) and the variation in this size range seems completely irregular. Nevertheless, the kinetic rates keep a general even odd oscillation up to Ag₆₉⁻. Most of Ag_n⁻ (even n) are reactive, and most of Ag_n⁻ (odd n) have very low reactivity or completely inert. This phenomenon can only be interpreted based on the alternating spin states of Ag_n⁻, which provides an evidence for the separate effect of spin accommodation in size range up to nano sizes. For Ag_n⁻ (n ≥ 70), their peaks become very broad because of the two isotopes of silver. The overlaps of Ag_n⁻ and Ag_nO₂⁻ make it impossible to distinguish where the

oscillation trend, i.e. the spin effect vanishes.

3.4 High electron binding energies correlate with low reactivity

In Fig. 2 and 4a, there are some inert even sized clusters Ag_n⁻ (n = 32, 46, 54, 56 and 58), which do not comply with the general oscillation trend caused by the spin alternation. As shown in Fig. 4b, all these clusters have electron binding energies higher than a threshold level of ~3.0 eV. From the viewpoint of spin accommodation, adsorption of O₂ on these even sized clusters is a barrier free process and should be very fast. Nevertheless, their high electron binding energies result in insufficient electron transfer to O₂ and thus the weak bond strength. If the bond energy with O₂ can't compensate the decrease of entropy in adsorptions, the processes will not happen. This analysis can reasonably interpret the inertness of Ag_n⁻ (n = 32, 46, 54, 56 and 58), while puts forward one question for an even sized cluster, Ag₄₈⁻. In the electron binding energies reproduced from ref [16] (shown in Fig. 4b), that of Ag₄₈⁻ is higher than the proposed threshold level (3.0 eV) and even higher than those of the inert Ag_n⁻ (n = 46, 54 and 56). Why does Ag₄₈⁻ still have high reactivity with O₂? By referring to the Fig. 8 of ref [16], we found there are some weak but clear bands at the low binding region of the spectrum of Ag₄₈⁻ (about 0.2-0.3 eV lower than the determined photodetachment threshold).¹⁶ These bands are very likely real signals, and then the electron binding energy of Ag₄₈⁻ (i.e. electron affinity of Ag₄₈) should be lower than the previously reported value and the threshold level (~3.0 eV) for O₂ adsorption proposed in this work. In a word, there is a good correlation between the electron binding energies and the reactivity of all even sized Ag_n⁻ with n ranges from 6 to 69. This correlation is a typical performance of the electron transfer mechanism for O₂ adsorptions. The overlaps of Ag_n⁻ and Ag_nO₂⁻ (n ≥ 70) and the lack of electron binding energies of Ag_n⁻ (n > 60) prevent us from analyzing the effect of electron binding energies on even larger sizes.

3.5 Is Ag₄₉⁻ an exception?

It is worth noting that there is a special size, Ag₄₉⁻, seeming to be an exception in the regular pattern in Fig. 2 and Fig. 4. With even number of electrons, the Ag₄₉⁻ is expected to have low reactivity according to the spin accommodation mechanism. On the contrary, the kinetic rate of Ag₄₉⁻ is the highest one in all Ag_n⁻ with n > 27, and additionally is the only odd size with higher reaction rates than both of its even sized neighbors. The electron binding energy of Ag₄₉⁻ in Fig. 4b is also out of expectation. We know that Ag₄₉⁻ has totally 50 valence electrons, which could form a close shell of 1S²1P⁶1D¹⁰2S²1F¹⁴2P⁶2D¹⁰ according to the free electron shell model.⁴⁶ This model predicts that the electron binding energy of Ag₄₉⁻ is a local maximum in the range from Ag₃₄⁻ to Ag₅₀⁻.¹⁶ However, the experimental electron binding energy of Ag₄₉⁻ is the lowest one in a wide size range of n > 36. The abnormalities of both the reactivity and the electron binding energy lead to an assumption that Ag₄₉⁻ is possibly not on its singlet state. The high spin state of Ag₄₉⁻, for example a triplet diradical, can endow this cluster with low electron bonding energy and high reactivity with O₂. This high spin

state can be caused by either a structure with a high symmetry, which has degenerate HOMOs, or a structure with a very low symmetry, causing very closely spaced electronic states near the Fermi level. More precise photoelectron spectroscopy and theoretical calculations could possibly give the exact electronic state and geometrical structures of Ag_{49}^- in future.

4. Conclusions

In summary, the current work studied the reactions of O_2 and Ag_n^- ($n = 6-69$), whose sizes range from several atoms to dimensions around 1 nm. The experiments obtained their relative rates at low temperature of 120K. The rate variation in the whole considered size range was well rationalized according to their electronic properties. The effects of two fundamental mechanisms, the spin accommodation and the electron transfer, were separately distinguished. The results unambiguously show that the reactions of O_2 with large silver clusters around 1 nm are still dominated by their global electronic properties, and local structural details have minor or negligible effects. This conclusion is of conceptual importance to understand the crucial O_2 activation process on silver nano catalysts.

Figure Captions

Figure 1

The schematic experimental setup. See context for description.

Figure 2

Mass spectra of the parent and product ions for reactions of Ag_n^- and O_2 with O_2 flow of 0.000 sccm, 0.035 sccm and 0.213 sccm, respectively. The top panel shows the spectra covering the size range of Ag_n^- ($n = 6-39$) and the bottom panel shows the amplified spectra ($\times 2$) covering size range of Ag_n^- ($n = 40-81$). The numbers of atoms in even sized clusters are labeled on top of each panel. The products Ag_nO_2^- are labeled using empty circle symbols and the products Ag_nO_4^- are labeled using solid circle symbols. The dot lines indicate the reactive even-sized ones, and the dash lines indicate the inert even-sized ones.

Figure 3

Linear fitting of $-\ln(I/I_0)$ vs O_2 flow rates for Ag_{10}^- , Ag_{24}^- , Ag_{31}^- and Ag_{49}^- . The I and I_0 stand for the normalized parent ion intensities at certain O_2 flow rate and without O_2 , respectively. The slope and relative rate (scaled to that of Ag_{10}^-) of each size are indicated.

Figure 4

The top panel shows relative kinetic rates for adsorption of O_2 on Ag_n^- ($n = 6-69$). The calibrated kinetic rate for Ag_{10}^- and the low limit of this measurement are indicated. The bottom panel shows the electron bonding energies of Ag_n^- (i.e. photodetachment energies) from ref [16] (■) and those from ref [17] (□). The values from ref [16]

were determined using the threshold of each spectra (ADE) while those from ref [17] were determined using the maximum of the first peak (VDE). The dashed line indicate the level of 3.0 eV, which is considered as a threshold to shut the O_2 adsorption reaction. Refer to context for details.

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