Formation of di-oxygen species on Ag anion clusters

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Abstract

Experiments using vibrationally resolved ultraviolet photoelectron spectroscopy show that oxygen selectively adsorbs on even-numbered Ag anion clusters, whereas the odd-numbered clusters are not chemically active. We provide evidence that O₂ molecularly adsorbs on Ag anion clusters consisting of less than 15 atoms. O₂ adsorption pattern for Ag anion clusters is quite analogous to that of Au anion clusters. We suggest that for the reactions efficiently catalyzed by Au-nanocatalysts, Ag nanoclusters can be a promising candidate as a building block of catalysts.

Since gold (Au), known as an inert material as bulk form, was found to become active with a cluster size below 3–4 nm, extensive studies have been performed to obtain a better understanding on catalytic process on Au clusters [1–9]. In surface chemistry, previous studies on Au-based catalysts have been often performed using model catalysts consisting of metal particles on well-ordered oxide surfaces with relatively broad particle size distributions [1–3]. Recently, mass-selected clusters were deposited onto the oxide surfaces to create mono-dispersed metal clusters, which is required to better understand the cluster size dependent changes of catalytic activities [4,5]. On MgO(1 0 0) surfaces, Au clusters consisting of between 8 and 20 atoms turned out to efficiently catalyze CO-oxidation, whereas smaller Au clusters are catalytically inert [4]. In combination with density functional theory (DFT) calculations, it was suggested that Au clusters interacting with F-centres of MgO(1 0 0) are responsible for the high catalytic activities towards CO-oxidation as a consequence of the charge transfer from F centres to Au clusters [4]. These results are in line with previous studies for Au-islands grown on TiO₂(1 1 0), which suggested that the oxygen vacancies of TiO₂ can lead to the charge transfer to yield negatively charged Au particles [6].

Recently, gas-phase Au anion clusters appeared to be suitable model system to shed light on reaction mechanisms of Au-nanocatalysis [7–9]. The Au anion clusters in the gas phase were shown to be chemically as active as deposited Au particles [8]. Studies on anionic clusters of Au are also relevant for Au-based catalysts consisting of Au particles and oxide supports, taking into account that the active gold particles in heterogeneous catalysis are negatively charged [17–19]. Studies for the O₂ adsorption on free Au anion clusters identified molecularly bound oxygen at room temperature, which was suggested to be important intermediate species in many reactions efficiently catalyzed by Au nanoclusters [9]. It is remarkable that the important reaction intermediate such as di-oxygen species, which was so far difficult to identify using surface analysis tools, can be detected employing experimental techniques of cluster physics. This result implies that combinations of surface chemistry and cluster physics are promising strategy to unveil reaction mechanisms of the reactions catalyzed by nanoparticles. It is also important to mention that comparison of gas phase data and results from deposited clusters can shed light on the metal-support interaction, which is one of the most important subjects in heterogeneous catalysis.

The increased catalytic activities of particles with confined sizes seem to be not limited to Au, but also relevant for other materials. For example, Ag nanoparticles

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were found to show similar catalytic activities to those of Au clusters for the partial oxidation of hydrocarbons and low temperature CO-oxidation, implying that high catalytic activities of small nanoparticles can be also relevant for other coinage metal clusters such as Ag and Cu [10]. Therefore, studies on chemisorption of Ag and Cu gas phase clusters can provide important information to better understand catalytic process of Ag- and Cu-based nanocatalysis.

In the present work, studies for O_2 adsorption on Ag anion clusters in the gas phase are carried out. Similar to the Au anion clusters, even/odd alterations were observed for the O_2 adsorption on Ag anion clusters, i.e. even numbered Ag anion clusters are generally active towards O_2 adsorption, whereas the odd-numbered cluster are not [7–9,11]. Ultraviolet photoelectron spectroscopy (UPS) spectra on $Ag_nO_2^-$ (n =number of Ag atoms) clusters show that oxygen is non-dissociatively bound on Ag anion clusters. These results are quite analogous to those from Au anion clusters [9], suggesting that Ag nanoclusters can be as active as Au nanocatalysts for those reactions, for which stabilization of activated di-oxygen species is important.

To synthesize $Ag_nO_2^-$ (n =number of gold atoms), Ag clusters were produced in the pulsed arc cluster ion source (PACIS), and subsequently exposed to O_2^- [12,13]. The temperature of the clusters is estimated to be room temperature. The mass of clusters was selected using a time-of-flight (TOF) mass spectrometer, and the UPS spectra of the mass-selected clusters were taken using UV laser pulse (photon energy = 4.66 eV).

In Fig. 1, TOF mass spectra collected for the Ag anion clusters after reaction in O_2 environments are displayed. Upon reacting with O_2 , the peaks corresponding to the Ag_n^- with n =even numbers become smaller, whereas the peak intensity of the respective $Ag_nO_2^-$ clusters increases. In Fig. 1, it is evident that Ag_{16}^- and Ag_{18}^- are less active than other even-numbered Ag anion clusters. The peaks of the odd-numbered Ag anion clusters do not change upon exposing to O_2 , indicating that these clusters are inert towards O_2 adsorption under these experimental conditions. The even/odd alteration in O_2 chemisorption reactivity has been already found for Au and Ag anion clusters in previous studies [7–9,11]. It is interesting to note that the even/odd alteration in the oxygen adsorption reactivities can be still observed for the clusters consisting of more than 30 atoms in Fig. 1 (except Ag_{32}^-), which is quite different from the result of Au anion clusters. Note that the Au anion clusters larger than Au_{20}^- are inert towards O_2 adsorption [9].

The even/odd-alteration for the O_2 adsorption on the Au anion clusters has been explained within an electronic model [7–9]. The even-numbered Au anion clusters show lower electron affinities with respect to the odd-numbered neighbours [14]. The Au anion clusters

Fig. 1. Mass spectra of the Ag anion clusters after reaction with O_2^- . The grids correspond to the masses of the bare Ag anion clusters. The top trace displays the Ag anion clusters with lower masses, whereas the bottom one corresponds to the larger clusters. Note that only even-numbered Ag anion clusters react with O_2^- .

with lower electron affinities can facilitate the electron transfer to O_2 , resulting in higher reactivities towards O_2 adsorption. In contrast, the clusters with higher electron affinities cannot lead to the charge transfer to the adsorbates, decreasing the O_2 adsorption activities. Au anion clusters larger than Au_{20}^- are inert towards O_2 adsorption, which can be also explained by higher electron affinities of these larger clusters.

It seems to be reasonable that the Ag anion clusters show even/odd-behaviours for the O_2 adsorption (Fig. 1), analogous to the case of Au, since the zig-zag pattern of the electron affinities as a function of cluster size can be also found for Ag [14]. Our observation that Ag_{16}^- and Ag_{18}^- are less reactive than other even-numbered neighbours also reconciles the relatively high electron affinities of these clusters. However, it is important to note that the absolute electron affinities of Ag anion clusters are generally significantly lower than those of Au anion clusters with similar sizes [14]. The electron affinities of the even-numbered Au anion clusters consisting of less than 20 atoms, which are active towards

O_2 adsorption, are lower than 3.4 eV, whereas the inactive Au anion clusters have electron affinities above 3.4 eV [14]. The electron affinities of Ag_n^- with $n =$ even and odd numbers are at highest 3.2 eV [14]. Assuming that the absolute electron affinity is the criterion for the reactivity towards O_2 adsorption, then not only even-numbered but also odd-numbered Ag anion clusters should be reactive towards O_2 adsorption. Our experimental observation for the even/odd behaviours of the Ag clusters towards O_2 adsorption suggests that the absolute electron affinities cannot be a sufficient criterion to determine the reactivity towards O_2 adsorption.

In spite of much higher electron affinities of Au anion clusters with respect to the respective Ag anion clusters, Au and Ag anion clusters consisting of less than 21 atoms show similar activity pattern towards the O_2 adsorption. This result can be interpreted in terms of strong d characters in the valence band of the Au clusters. Previous quantum calculations have found very strong d-sp mixing for Au, and the UPS spectra of the pure Au anion clusters also agree with these calculations [14–18]. In contrast to Au, Ag valence band exhibits more or less pure sp-characters. It is possible that d orbitals play an important role for the chemisorption of O_2 , since the d-orbitals can overlap better with O_2 $2\pi^*$ orbitals with respect to the sp-states due to the symmetry reason. Because of the larger d-characters in the valence electronic levels of Au anion clusters, even-numbered Au anion clusters can be as reactive as Ag anion clusters for O_2 adsorption, in spite of relatively high electron affinities of even-numbered Au anion clusters with respect to those of the respective Ag anion clusters.

To shed light on structural properties of $Ag_nO_2^-$, UPS experiments were carried out (Fig. 2). Electron affinities of the most of the Ag anion clusters displayed in Fig. 2 are shifted to higher binding energies by 0.5–0.9 eV upon O_2 adsorption [14]. For Ag_2^- and Ag_8^- , the O_2 adsorption results in increase of the electron affinities by 1.3 eV, which is larger than in the case of other Ag anion clusters [14,19]. Oxygen acts as an electron-withdrawer, and the increase of the electron affinities by O_2 adsorption is comparable to those of Au anion clusters (0.6–1.1 eV) [20]. Note that dissociative adsorption of O_2 should result in a larger increase of the electron affinities with respect to the molecular adsorption, since in a simple model, O_2 is one-electron-acceptor, whereas two oxygen atoms formed by dissociative adsorption of O_2 withdraw four-electrons from metals. Similar changes in electron affinities for Ag and Au anion clusters upon O_2 adsorption suggest that the adsorption structures of O_2 on Au and Ag anion clusters can be similar, i.e. O_2 molecularly adsorb on these Ag anion clusters [9,20].

Only for $Ag_2O_2^-$ and $Ag_8O_2^-$, periodic structures are observed in the UPS spectra corresponding to about

Fig. 2. UPS spectra of the Ag anion clusters reacted with O_2^- (photon energy = 4.66 eV). Vibrational fine structures are denoted with arrows.

170 meV, which can be assigned to the stretching frequency of O–O (Fig. 2) [9]. Note that the periodic structures of the UPS of anions correspond to the vibration quantum of the neutral states with identical geometries to those of the anionic counterparts (Franck–Condon profile). Observation of the O–O stretching frequency at the lower binding energy regimes in the UPS spectra of $Ag_2O_2^-$ and $Ag_8O_2^-$ indicates that the detachments of the electrons with the lowest binding energies in $Ag_2O_2^-$ and $Ag_8O_2^-$ change the O–O distance significantly. This implies that the excess electron in the anionic state should be localized in O_2 , i.e., superoxo-species (O_2^-) are formed in this case. For other clusters without the vibrational fine structures in the UPS spectra, the excess electrons in the anionic states are rather delocalized in the clusters. As mentioned above, the electron affinities of Ag_2^- and Ag_8^- increase upon O_2 adsorption by about 1.3 eV, which is significantly larger than the values for other Ag anion clusters in Fig. 2. This result also reconciles larger Ag $\rightarrow O_2$ charge transfers for Ag_2^- and Ag_8^- with respect to the other Ag anion clusters in Fig. 2. The larger charge transfer for Ag_2^- and Ag_8^- to O_2 can be rationalized within the electronic shell model. By removing one electron from the Ag_2^- and Ag_8^- , the closed shell structures ($1s^2$, or $1s^21p^6$) can be formed [20]. It is worth mentioning that we cannot rule out the possibility that oxygen partially dissociates on Ag anion clusters forming less abundant isomers, which are not much pronounced in the UPS spectra. In the present work, we focus on those isomers governing the low binding energy part of the UPS

spectra, and the existence of different isomers is a subject of a forthcoming Letter.

We provide spectroscopic evidence that O_2 is molecularly bound on Ag_2^- and Ag_8^- clusters. Other Ag anion clusters in Fig. 2 show less $Ag \rightarrow O_2$ charge transfers with respect to the case of Ag_2^- and Ag_8^- , which is evident from the electron affinity changes and the absence of vibrational fine structures corresponding to the O–O stretching mode. Considering that dissociative adsorption requires much larger charge transfer from metal to $O_2-2\pi^*$ orbital, oxygen should be also molecularly bound on other Ag anion clusters in Fig. 2.

It is interesting to note that striking similarities between the UPS spectra of $Ag_nO_2^-$ with those of $Au_nO_2^-$ can be eventually found (Fig. 3). For $Ag_2O_2^-$ and $Au_2O_2^-$, broad features can be found at lower binding energies followed by several narrower peaks. For $Au_{12}O_2^-$ and $Ag_{12}O_2^-$, three distinct peaks are observed at the lower binding energy regimes. The valence band structure of these clusters are most likely dominated by the antibonding orbitals of oxygen ($O_2-2\pi^*$), suggesting that the adsorption structures of O_2 on these Au and Ag anion clusters are very analogous. These results again suggest that oxygen should be molecularly bound on these Ag anion clusters, like on Au anion clusters.

Larger Ag and Au clusters behave chemically completely differently, i.e. Au anion clusters larger than Au_{20}^- are inert towards O_2 adsorption, whereas the Ag clusters consisting of more than 20 Ag atoms are still reactive. However, the O_2 adsorption patterns on Ag anion clusters in Fig. 2 are quite analogous to the case of the respective Au anion clusters. It should be emphasized that Au anion clusters smaller than Au_{20}^- recently draw particular attention due to their extraordinarily high catalytic activities for those reactions, which involve

oxygen adsorption. Based on our results, it is likely that that Ag-nanoclusters can be as active as Au-clusters for those reactions for which molecular oxygen is an important intermediate, for example CO-oxidation and partial oxidation of hydrocarbons [10].

We provide evidence that oxygen selectively adsorbs on even-numbered Ag anion clusters, whereas the odd-numbered clusters are not chemically active, which is quite analogous to Au. Oxygen molecularly adsorbs on Ag anion clusters consisting of less than 15 atoms, forming superoxo-species, which is quite analogous to the results from the Au anion clusters with similar sizes. These results indicate that molecular adsorption of O_2 at room temperature can be common phenomena for small coinage metal cluster anions. We suggest that for the catalytic reactions, for which molecular oxygen is an important reaction intermediate, not only Au but also Ag nanoclusters can be a possible candidate.

Acknowledgements

DFG (Deutsche Forschungsgemeinschaft) is acknowledged for the financial support.

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Fig. 3. UPS spectra of $Ag_nO_2^-$ and $Au_nO_2^-$ are compared for $n=2,12$. For $Ag_nO_2^-$ the photon energy of 4.66 eV was used for the UV-pulse, whereas for $Au_nO_2^-$ 6.4 eV photon was used due to higher electron affinities of these clusters.