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Origin of unusual catalytic activities of Au-based catalysts

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Abstract

Experimental evidences for the non-dissociative chemisorption of O_2 are presented on even-numbered free Au anion clusters (Au_n^-, n = number of atoms) up to Au_{20}^- at room temperature. Our result indicates that the formation of the activated di-oxygen species is the key of the unusual catalytic activities of Au-based catalysts. No correlation between geometrical structures of Au_n^- and the activities towards O_2 adsorption was found, showing that site-specific chemistry disappears for Au-nanocatalysis. We demonstrate that interplay between cluster physics and surface chemistry is a promising strategy to unveil mechanisms of elementary steps in nanocatalysis.

1. Introduction

Pioneering works of Haruta, Goodman and many other scientists [1–7] in the last decade have shown that oxide-supported gold (Au) particles, which are inert as bulk form, become extraordinarily active for various chemical reactions with a cluster size below two to three nanometers. The unusual size-dependent catalytic behaviors of Au clusters are currently one of the most widely treated subjects in chemistry and physics [1–23]. However, the origin of the exceptional catalytic properties of Au nanoclusters is still questionable. For O_2 adsorption on Au particles, which is responsible for the cluster-size effects of Au-based catalysts, various adsorption structures such as dissociative adsorption and the formation of superoxo-species and peroxo-species have been under consideration [3,7–12]. However, no generally accepted picture for the O_2 adsorption on Au-nanoclusters has appeared yet.

Combination of density functional theory (DFT)-calculations and various spectroscopic experiments concluded that the electron transfer from oxide supports to Au is crucial for the high catalytic activities [7]. The mass-selected Au anion clusters (Au_n^-, n = number of gold atoms) in the gas phase show comparable catalytic activities to those of oxide-supported Au particles, confirming the importance of the negative charge on Au clusters for catalytic activities [10]. Investigations on gas phase clusters are advantageous, since the mass of free anion cluster is better controlled with respect to the deposited clusters, allowing studies on cluster-size dependence for the electronic, geometric and chemical properties with an atomic

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precision. Thus, Au_n^- in the gas phase was suggested to be used as model systems to unveil reaction mechanisms of Au-nanocatalysts [9–11].

In this Letter, we open a new insight into the elementary chemisorption steps on Au-nanocatalysts using experimental techniques of cluster physics. We found that O_2 molecularly adsorb on Au_n^- with $n =$ even numbers up to Au_{20}^- at room temperature (with an exception for Au_{16}^-, which is inert towards O_2 chemisorption). Our results suggest that the di-oxygen species are important reaction intermediates for catalytic reactions on Au-based catalysts. We found that the most important criterion for strong interaction with O_2 for Au anion cluster is a low electron affinity. It is remarkable that the anion of Au_{20}, a 'magic' cluster with a large gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), interacts more strongly with O_2 with respect to other Au anion clusters larger than Au_8^-, due to the low electron affinity of Au_{20} [24]. This suggests that chemically inert 'magic' clusters can become catalytically active with one excess electron. No correlation between geometrical structures of Au_n^- and the activities towards O_2 adsorption was found, showing that site-specific chemistry disappears for Au-nanocatalysis. By comparing the results from Au_n^- in the gas phase and those of oxide-supported Au particles, general pictures for the characteristics of active Au-nanocatalysts and metal–support interactions are drawn.

To synthesize $Au_nO_2^-$ ($n =$ number of gold atoms), Au clusters were produced in the pulsed arc cluster ion source (PACIS) [11,25], and subsequently exposed to O_2. 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 ultraviolet photoelectron spectroscopy (UPS) spectra of the mass-selected clusters were taken using UV laser pulse (photon energy = 4.66 or 6.4 eV). AuO^- clusters can be also prepared by the reactions between Au clusters and atomic oxygen created by the dissociation of O_2 in the electric arc.

In Fig. 1 the mass spectrum for Au_n^- after reaction with O_2 is demonstrated. Au_n^- with $n =$ even numbers react with O_2 (with an exception of

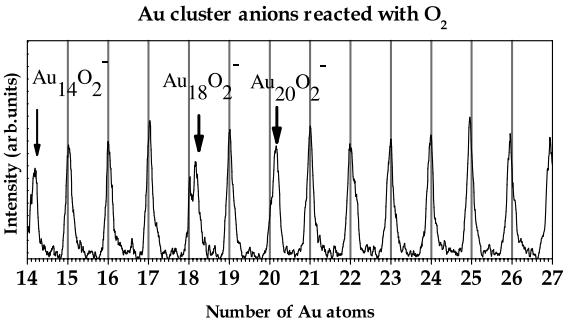

Fig. 1. Mass spectra of Au anion clusters after reaction with O_2. The grid lines correspond to the masses of the pure Au clusters. Peaks deviating from the grid lines correspond to the reacted clusters.

Au_{16}^-), whereas the odd numbered clusters are inert (with an exception of Au_1^- and Au_3^-, which partially react) [9–11,26]. Our results are in agreements with this previously observed even/odd-alteration in the O_2 adsorption reactivities, which follows the even/odd-pattern of the electron affinity (EA) of Au_n^- (EAs of even-numbered Au_n^- are lower than those of odd-numbered clusters) [9–11,26,27]. It is important to mention that Au_n^- with $n = 22, 24, 26\ldots$ do not react with O_2 at all, which can be explained by higher electron affinities of these clusters.

In Fig. 2, the UPS spectra of $Au_nO_2^-$ (produced in O_2 atmosphere) with $n =$ 2–8 taken using a laser with a photon energy of 4.66 eV are compared. UPS spectra for $Au_nO_2^-$ with $n = 2, 4, 6$ exhibit vibrational fine structures of about 150–180 meV corresponding to the O–O stretching frequencies, indicative of the non-dissociative adsorption of O_2. The vibrational frequencies in Fig. 2 are much higher than those found for the di-oxygen species on transition metal surfaces [28]. However, it is important to note that the vibrational frequencies in the UPS spectra correspond to those of neutral clusters with identical geometries to the respective anions. In the anionic states, the additional charge occupies the antibinding orbital of oxygen, further activating the O–O bonding, and decreasing the O–O stretching frequencies [11]. Thus, the O–O vibrational frequency of the anionic state should correspond to those of the peroxo (80–120 meV) or superoxo-species (135–150 meV) [11,28].

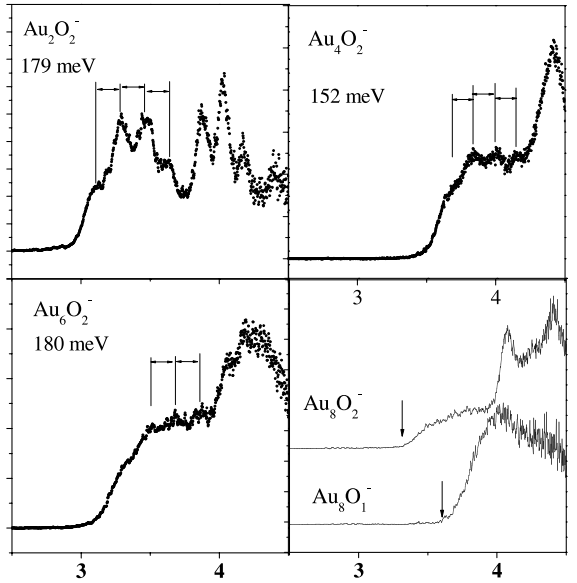

Fig. 2. UPS spectra of $A_nO_2^-$ for $n = 2, 4, 6, 8$, using a laser with a photon energy of 4.66 eV. For $n = 2, 4, 6$, vibrational fine structures are resolved, which correspond to the stretching frequencies of di-oxygen species. For $n = 8$, no vibrational structures are resolved, however, comparison of the UPS spectra from Au_nO^- and $Au_nO_2^-$ allow to determine that oxygen molecularly adsorb on Au_8^-.

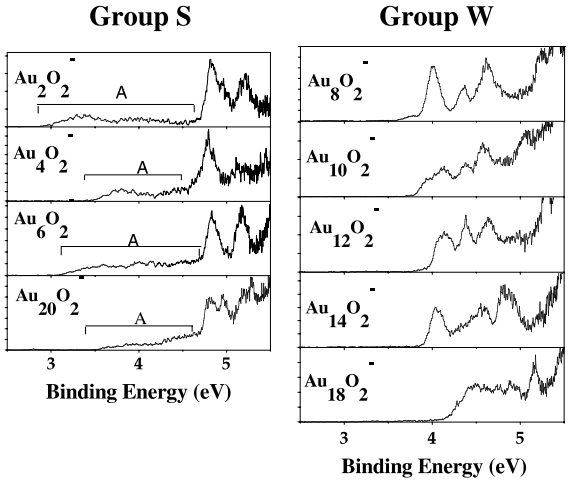

Fig. 3. Left: UPS spectra of $Au_nO_2^-$ for $n = 2, 4, 6, 20$. Right: UPS spectra of $Au_nO_2^-$ for $n = 8$–18. At the bottom, It is important to note that Au_n^- with $n = 8$–18 show higher electron affinities (<2.75 eV) to those of the Au_n^- with $n = 2, 4, 6, 20$.

For $Au_8O_2^-$, the vibrational fine structures are hardly resolved in the UPS spectrum. However, information on the adsorption structures of O_2 on Au_8^- can be obtained using electron affinities. In a simple electron transfer model, the formal charges of molecularly adsorbed oxygen are −2 (peroxo-species) or −1 (superoxo-species), and that of atomic oxygen is −2. For various $Au_nO_m^-$ (n,m = integers), the degree of the electron transfer from Au to oxygen can be arranged in the order of O_2 (superoxo, 1e transfer) < O_2 (peroxo, 2e), O (one oxygen atom, 2e) < 2O (two oxygen atoms).

A larger electron transfer from Au to adsorbates should lead to a higher electron affinity, i.e., by comparing the electron affinities of Au_nO^- with those of $Au_nO_2^-$, one can identify, if O_2 dissociate or not in $Au_nO_2^-$. Within this approach, a lower electron affinity of $Au_8O_2^-$ with respect to that of Au_8O^- indicates a molecular adsorption of O_2 (Fig. 3). The comparison of the electron affinities of $Au_nO_2^-$ and Au_nO^- for $n = 1, 2, 4, 6$ suggests that O_2 dissociatively adsorbs on Au^-, but molecularly on Au_2^-, Au_4^-, and Au_6^-. These results are in agreements with the vibrational fine structures of the UPS spectra (Fig. 2) as well as DFT-calculations [11,21], confirming that electron affinities can be used to determine adsorption structures of O_2 on Au_n^-. It is worth mentioning that molecular adsorption of O_2 on other transition metals such as anionic Cr monomer gives much less increase of the electron affinities with respect to the dissociative adsorption, also supporting our simple electronic model [29]. For larger clusters, measurements on monoxide become difficult due to a reduced resolution of the TOF mass spectrometer with increasing cluster size.

UPS studies using a laser with a photon energy of 4.66 eV are limited to the smaller clusters with $n > 10$, since the electron affinities of these larger clusters become very close to the photon energy. To obtain information on electronic structures of $Au_nO_2^-$ for n = up to 20 with a wider energy range, UPS spectra of $Au_nO_2^-$ are collected using a laser with a higher photon energy (6.4 eV). (Fig. 3) First, we focus on $Au_nO_2^-$ clusters with $n = 2, 4, 6$, 20 (these clusters are referred to as group S). The group S clusters generally show relatively low electronic affinities (EA < 2.75 eV) (Table 1) [27]. For the group S clusters, the distinct features of

the pure Au anion clusters existing at the binding energies below about 4.7 eV completely disappear upon O_2 adsorption, and broad features between 3 and 4.5 eV (marked with A in Fig. 3) appear, followed by several narrower peaks. These wide features A in Fig. 3 result from the combination of the O_2 $2\pi^*$-orbitals and the valence occupied molecular orbital (MOs) of Au_n^-. As mentioned above, O_2 molecularly adsorb on Au_n^- with $n = 2, 4, 6$ (Fig. 2). Based on the similarities in the valence electronic structures (Fig. 3), it can be suggested that O_2 is also molecularly bound on Au_{20}^-. The very large widths of the peak A are an evidence for a strong overlap of the O_2–$2\pi^*$ orbitals with the valence electronic levels of Au_n^-. Note that according to the Franck–Condon profile, a large structural change upon electron excitation results in broad band features. Electron detachment can lead to a large structural change, when this electron is involved in a strong chemical bonding in a cluster (in our case O_2–Au bonding). By comparing the UPS spectra of the $Au_nO_2^-$ with those of the respective pure Au anion clusters (Fig. 4), it becomes more obvious that the valence band structure of Au_n^- is completely changed upon O_2 adsorption, confirming significantly large interactions between O_2 and the group S clusters. It should be noted that not only HOMO but also other occupied MOs of Au anion clusters participate in the O_2 chemisorption (Fig. 3, Fig. 5). Most likely, approach of O_2 close to Au_n^- is facilitated by sufficient charge transfers from the delocalized sp-state (HOMO) to O_2–$2\pi^*$ orbital, which then enables the contributions of other localized MOs of Au_n^- with higher binding energies in the O_2 chemisorption.

Table 1
The electron affinities of Au_n^- and $Au_nO_2^-$ are summarized

n	EA of Au_n^-	EA of $Au_nO_2^-$
2	1.7	3.0
4	2.6	3.5
6	2.1	3.2
8	3.0	3.6
10	2.8	3.8
12	3.0	3.8
14	2.8	3.9
18	3.1	4.1
20	2.7	3.6

Electron affinities are given in eV. n corresponds to the number of gold atoms in a cluster.

In contrast to the case of group S clusters, UPS spectra of $Au_nO_2^-$ with $n = 8$–18 (group W) consist of distinct multiple peaks (Fig. 3). The peaks from the HOMO of Au anion clusters disappear upon O_2 adsorption, however, in contrast to the case of the group S, no broad feature is observed in the binding energy regime between 3 and 4.5 eV. Only distinct peaks above 4 eV existing in the UPS spectra of the pure Au anion clusters are still visible with minor modifications after O_2 adsorption (Fig. 4) [27]. This suggests that a charge transfer from the HOMO of Au anion clusters to the oxygen is the main chemisorption mechanism, whereas additional overlap between O_2–$2\pi^*$ orbitals and other MOs of the Au anion clusters is

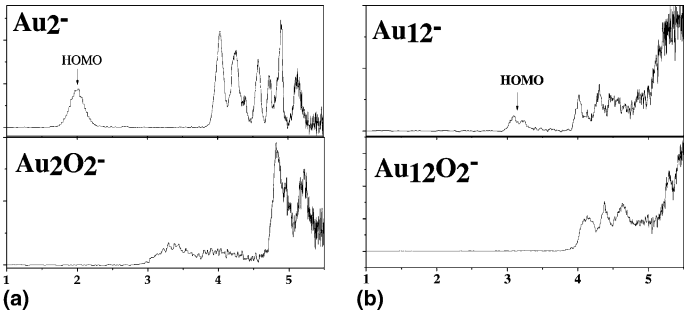

Fig. 4. (a) As a representative of the group S clusters in Fig. 3, UPS spectra of Au_2^- and $Au_2O_2^-$ are compared to clarify the changes induced by oxygen adsorption for the group S clusters. (b) As a representative of the group W clusters in Fig. 3, UPS spectra of Au_{12}^- and $Au_{12}O_2^-$ are compared to clarify the changes induced by oxygen adsorption for the group W clusters.

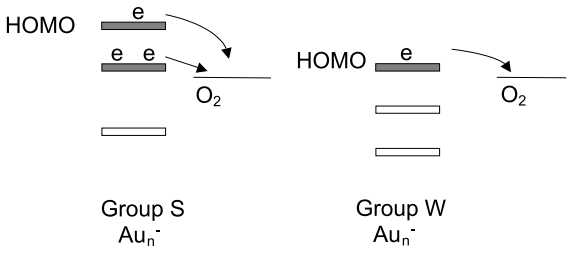

Fig. 5. Simplified orbital schemes for the interactions between O_2 and Au anion clusters.

negligibly small, which is quite different from the result of the group S clusters (Fig. 5). This result is evidence for the much weaker interactions between O_2 and group W clusters with respect to the group S clusters. General trend for the weaker interactions of group W clusters with O_2 is consistent with the recent results from O_2 adsorption reactivity experiments on Au anion clusters [9]. Much weaker interactions between O_2 and group W clusters imply that O_2 should not dissociate on these Au anion clusters, since for the dissociative adsorption, stronger Au–O_2 interactions are required. Changes of the electron affinities of the W group clusters upon O_2 adsorption are similar to the case of the S group clusters, also suggesting molecular adsorption of oxygen on group W Au anion clusters (Table 1). That the Au anion clusters in group W react more weakly with O_2 than group S clusters is explained by lower electron affinities of group S clusters with respect to those in the group W [27]. Within a simple charge transfer model, one can argue that W group clusters allow less $Au \rightarrow O_2$ charge transfer than S group clusters.

It is interesting to note that O_2 adsorption mechanism on Au_{20}^- is much different from those of other Au anion clusters with similar sizes (Au_n^- with $n > 8$), and rather analogous to O_2 adsorption pattern of much smaller clusters ($n = 2, 4, 6$). Recently, Au_{20} was shown to have a highly symmetric tetrahedral structure with an extremely large HOMO–LUMO gap, i.e. Au_{20} is classified as 'magic' cluster, suggesting that Au_{20} should be chemically inert [24]. In general, 'magic' clusters tend to exhibit relatively low electron affinities (note that the electron affinity of C_{60} is even lower than that of Au_{20}) [30], since the energy level of LUMO is shifted to the lower energy range as a consequence of a large HOMO–LUMO gap. The strong interaction with Au_{20}^- with O_2 indicates that a 'magic' cluster can become chemically very active with an excess electron, triggering further studies on chemical activities of other 'magic' clusters with one excess electron. It should be emphasized that it is not only the one additional electron in the HOMO of the anionic state of the 'magic' cluster, which participate in the chemisorption. Other MOs in the higher binding energies, which should be chemically inert in the neutral state participate in the chemisorption in the anionic state (Fig. 3).

It should be pointed out that the 2D to 3D transitions of the Au anionic clusters take place at a cluster size of Au_{13}^- [31] leading to a highly symmetric tetrahedral (pyramid shape) structure for Au_{20}^- [24]. The change of the cluster geometry as a function of size is not reflected in the O_2 chemisorption pattern in the present work, indicating that for Au-nanoclusters, site-specific chemistry is absent. It is likely that absence of the size-specific chemistry can be also relevant for other metal nanoclusters.

Comparison of chemisorption properties of Au_n^- with those of Pt-group metal surfaces provides insights into the origin of the unusual catalytic properties of gold nanoclusters for CO-oxidation and propylene epoxidation. On Pt-group metal surfaces, CO oxidation usually takes place through the Langmuir–Hinshelwood mechanism, in which O_2 first dissociates and then reacts with CO to form CO_2 [32]. On Au anion clusters, in contrast, the stabilization of the activated molecular oxygen at room temperature can open new reaction channels (e.g., CO-oxidation mediated by carbonate-like species) [4], responsible for the low temperature CO-oxidation. Molecular adsorption of oxygen can play a vital role for the enhanced activities of gold clusters towards many other catalytic reactions such a partial oxidation of propylene, in which formation of hydroperoxide is suggested to be important [13].

Comparison of the gas phase data and those of the Au particles on TiO_2 can provide a better insight into the role of the support materials in the Au-nanocatalysis. We suggest that support materials in Au-nanocatalyis play the following roles.

1. Charge transfers from support materials to the Au particles take place, leading to the increase of the catalytic activities. The gas phase data in the present work indicate that the negative charge on the Au clusters is crucial for the high reactivities. X-ray photoelectron spectroscopy (XPS) results from Au particles on TiO_2 in combination with DFT calculations are also in line with the negative charging of the chemically active Au particle by oxygen vacancies of TiO_2 [23].
2. Electronic and geometric structures of Au particles are significantly changed by TiO_2. In the gas phase, the HOMO–LUMO gaps of the clusters becomes negligibly small, when the clusters consist of more than about 25–30 atoms [27]. The cluster shape becomes already three-dimensional at a cluster size of A_{20}. In contrast, Au strongly wets the TiO_2 surfaces, keeping the confined thickness of larger clusters to the direction normal to the oxide surface (Au initially grows two-dimensional), which increases the contact area between Au and TiO_2 [3]. As a consequence of this metal-support interaction, Au particles consisting of several hundred Au atoms (about 2–3 nm in diameter) are still semiconductive with band gaps up to 1.2 eV [3]. As aforementioned, a larger band gap (or HOMO–LUMO gap) of a nanoparticle can cause a lower electron affinity, leading to a higher chemical activity towards O_2 adsorption. This can rationalize, why the mean size of catalytically active Au particles on TiO_2 is much larger than that in the gas phase without support.

In summary, we have shown that high chemical activities of Au nanoclusters result from the stabilization of molecular oxygen on negatively charged Au clusters with relatively low electron affinities. Interactions of Au anion clusters with O_2 increases with reduced electron affinity. In particular, the anion of Au_{20}, which is a magic cluster with a large HOMO–LUMO gap, becomes more active than other neighboring Au anion clusters towards O_2 chemisorption, indicating that other 'magic' clusters with large HOMO–LUMO gaps are good candidates for building blocks of heterogeneous catalysts with one excess electron. No evidence for the site-specific chemistry was found, and absence of the site-specific chemistry can be relevant for other nanoclusters. We demonstrate that interplay between cluster physics and surface chemistry is a promising strategy to unveil mechanisms of elementary steps on various nanocatalysts. Moreover, a direct comparison between the data from gas phase clusters and supported particles provides a better understanding for the metal–support interactions.

Acknowledgements

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