

Interaction of Pd cluster anions (Pd_n^- , $n < 11$) with oxygen

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Abstract. Interactions between oxygen and Pd cluster anions were studied using Time-of-Flight (ToF) mass spectrometry and Ultraviolet Photoelectron Spectroscopy (UPS). In contrast to the coinage metal clusters, no pronounced size selectivity towards chemisorption of oxygen molecules can be observed for the Pd cluster anions: regardless of the cluster size, no more than 2 oxygen molecules can be attached to a cluster. When Pd_nO_m^- clusters are prepared by pre-dissociation of oxygen molecules by electric arc and post-reaction with Pd, the proportion of Pd cluster anions reacted with oxygen does not much change compared to the case of the reaction between Pd cluster anions and O_2 molecules. This result indicates that the O_2 chemisorption on Pd cluster anions does not involve large activation barriers: using different synthesis method of a cluster, one can get a better insight into the chemisorption routes of molecules on metal clusters.

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1 Introduction

For small metal clusters consisting of less than ~ 100 atoms, every additional atom can significantly alter chemical properties of the clusters. A sudden jump of the nitrogen uptake of W clusters can be found as the number of W atoms in a cluster exceeds 15 [1,2]. For Ti cluster anions, a transition from molecular to dissociative chemisorption of hydrogen can be found as the number of atoms in a cluster becomes larger than 4 [3]. Ag cluster anions consisting of less than ~ 40 atoms show an even-odd alteration of the O_2 chemisorption reactivity, i.e. only even-numbered cluster anions can react with O_2 [4]. For Au, a similar even-odd pattern for the oxygen uptake can be observed in the cluster size regime below 21 atoms [5–7]. Cu cluster anions smaller than 5 atoms can dissociate molecular oxygen, whereas larger ones can show non-dissociative chemisorption of oxygen [8–11]. As a consequence of these unique chemical properties of small clusters, enhanced catalytic activities can often be found for smaller clusters, which are absent for the respective bulk materials. For example, Au is catalytically inactive as bulk, whereas Au nanoclusters can show very high catalytic activities for various reactions such as CO-oxidation and partial oxidation of hydrocarbons [12–14]. A similar size-selectivity in heterogeneous catalysis can exist in the case of other transition metals [15].

The size dependent changes of the chemical properties of the clusters can be attributed to either electronic or geometric effects. In terms of electronic structure, each additional atom in a cluster can change electronic properties of clusters (such as electron affinity, or ionization potential), which has a large influence on their chemical properties. When a cluster has lower binding energies of valence electrons, the metal to adsorbate charge transfer can become easier, resulting in stronger metal cluster-gas molecule interactions [16,17]. Note that the chemisorption of diatomic gas molecules such as CO, O_2 , N_2 and H_2 with metal can roughly be explained by the charge transfer from the valence d orbitals of metal to the antibonding orbitals of the gas molecules [18]. In the electronic model, it is assumed that the site-specific chemistry does play only a minor role. Within the geometric model, in contrast, an increase of the number of specific adsorption sites as a function of cluster size is suggested to enhance the chemisorption reactivities of clusters [1,2].

The strong even-odd behaviors for the chemisorption reactivity of some coinage metal clusters mentioned above are related to the even-odd alteration of the number of electrons in the Highest Occupied Molecular Orbital (HOMO) of a cluster [19]. Here, we studied Pd clusters, one of the *d*-metal clusters, which do not show such an even-odd pattern of the electronic structure. In contrast to the *s*-metal clusters, electronic structures of the *d*-metal clusters are governed by high densities of states of *d* electrons close to the HOMO, and therefore, the electronic structures of the Pd cluster anions change rather gradually as a function of cluster size [20–22]. Chemisorption

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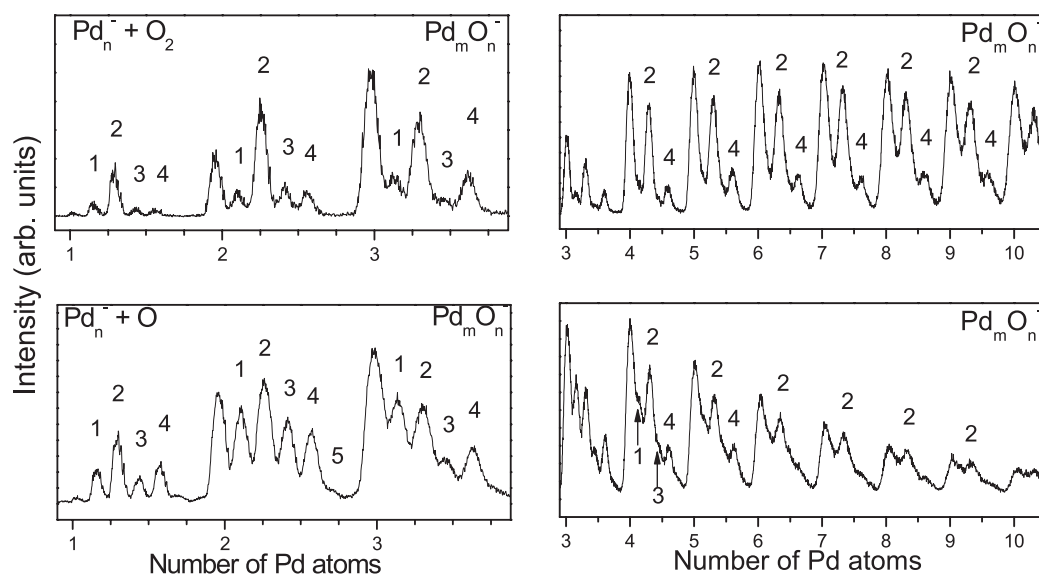


Fig. 1. Top: Pd cluster anions reacted with molecular oxygen, bottom: Pd cluster anions reacted with atomic oxygen.

of gas molecules on Pd single crystal surfaces as well as clusters has been studied in the past [23,24]. At room temperature, oxygen dissociatively chemisorbs on Pd single crystal surfaces. In the present work, no pronounced size-selectivity in chemisorption of oxygen could be observed, which can be related to the less pronounced size dependence of the electronic structures of the Pd cluster anions compared to those of the coinage metal clusters. Increase of the number of adsorption sites does not seem to play an important role for the chemisorption reactivity of oxygen.

2 Experimental details

To synthesize Pd_n^- and Pd_nO_m^- , Pulsed Arc Cluster Ion Source (PACIS) was used with He as buffer gas (purity better than 99.9999%) [25,26]. Two different methods, namely molecular and atomic oxygen methods, were used for the synthesis of reacted clusters. Details of both preparation methods can be found elsewhere [25,26]. It has been previously shown that Ultraviolet Photoelectron Spectra (UPS) of Cu_6O_2^- synthesized using two different methods are completely dissimilar, indicating that the concentration of molecular oxygen in the gas phase is negligibly small, or even if a significantly large amount of molecular oxygen should exist in this case, clusters react preferentially with atomic oxygen due to its much higher reactivity [8]. The temperature of the clusters at the UPS measurement stage is generally estimated to be room temperature. The mass of the 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).

3 Results and discussions

When the molecular oxygen method was used to prepare Pd_nO_m^- clusters, PdO_n^- peak ($n > 1$) could be found with

a significantly higher intensity than those of Pd^- and PdO^- in the mass spectra (Fig. 1). The abundance in the mass spectrum of anions depends on the stabilities of the clusters as well as the electron affinities of the respective neutral clusters [27]. The probability to catch an electron in the plasma of the source is higher for the species with a higher electron affinity. A Pd monomer anion reacted with oxygen should show a higher electron affinity of the neutral counterpart than that of the bare Pd monomer (also confirmed in our UPS studies in Figs. 3 and 4), resulting in the increase of the concentrations of the reacted clusters in the anionic mass spectra. Therefore, the higher intensity of PdO^- than that of Pd^- in the mass spectrum does not necessarily reflect a higher abundance of PdO^- than Pd^- in the cluster source. This result could come from the lower electron affinity of the Pd monomer, which reduces the concentration of the Pd monomer anions in our system. The intensity of Pd_2O_2^- is slightly higher than that of the respective bare Pd cluster anion. For larger Pd cluster anions, the bare Pd cluster peaks are generally larger than those of the respective Pd_nO_m^- clusters with $m = 2, 4$. The formation of PdO^- by using the molecular oxygen method can come from the formation of a PdO_2 cluster and subsequent ejection of an oxygen atom from this cluster, similar to the previous results on Ag-oxide clusters [28]. However, one cannot completely exclude the possibility of the formation of Pd-hydroxide clusters in this case.

It is interesting to note that regardless of the cluster size, no more than 5 oxygen atoms can be attached to a cluster under our experimental conditions. Within the model of the geometric structure dominating the chemisorption pattern, number of oxygen atoms reacted with Pd clusters should become larger with increasing number of Pd atoms in a cluster. This was not found in the present work, implying that the chemisorption pattern is most likely not governed by geometric structures of the clusters. Rather, the chemisorption seems to correlate with the electron affinities of the Pd clusters, which do not show a pronounced size-dependent variation.

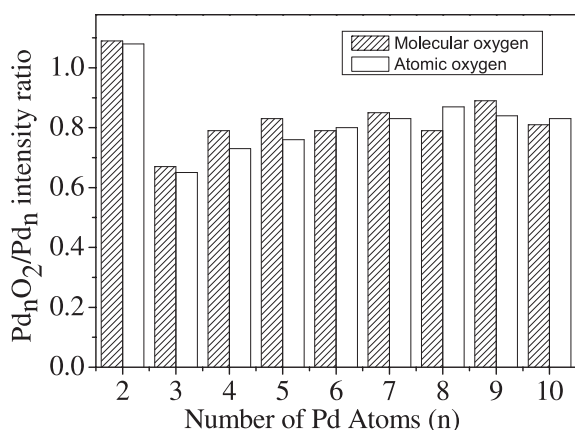


Fig. 2. The relative intensities of Pd_nO_2 peaks with respect to that of the respective Pd_n of the data in Figure 1 are summarized.

When the atomic oxygen method was used instead of the molecular oxygen method for the cluster preparation, the appearance of the Pd_nO_m^- clusters with $m = 1, 3$ could be found, which were almost absent using the molecular oxygen method. In general, the relative intensities of the $\text{Pd}_n\text{O}_2^-/\text{Pd}_n$ clusters do not change much depending on the preparation methods: when atomic oxygen was used, no significant increase of the relative amounts of reacted clusters could be found (Fig. 2). When there is a high activation barrier for the O_2 chemisorption on Pd cluster anions, then the relative concentrations of the Pd_nO_2^- cluster anions should significantly increase upon changing the preparation method from the molecular oxygen method to the atomic oxygen ones. Our data imply that the chemisorption of O_2 on Pd cluster anions is not much limited by high kinetic barriers under our experimental conditions.

In the case of the reaction of W_n^- clusters with atomic nitrogen, the even/odd pattern of the number of adsorbed N atoms disappears [29]. The adsorption of 2 and $4N$ atoms have about the same probability as those of 3 and $5N$ atoms to a W cluster anion. In contrast, slight preference of the attachments of even-numbers of oxygen atoms to the odd-numbers can be found for the reactions between atomic oxygen and Pd cluster anions (Fig. 1, lower right trace). Based on this result, one may argue that the Pd clusters ($n > 3$) have a propensity towards molecular chemisorption of oxygen.

Before measuring the UPS spectra of the reacted clusters, UPS studies were carried out for bare Pd cluster anions, which have shown a good agreement with previous studies of the same systems (data not shown here) [20–22].

The UPS spectra of the Pd_nO_2^- cluster anions with $n = 1-7$ prepared by the atomic oxygen method are shown in Figures 3 and 4. Upon attachment of two oxygen atoms to a cluster, the electronic structures are significantly changed. Most likely, orbitals of oxygen (either $2\pi^*$ from molecular oxygen or $2p$ for atomic oxygen) significantly contribute to the valence electronic structures

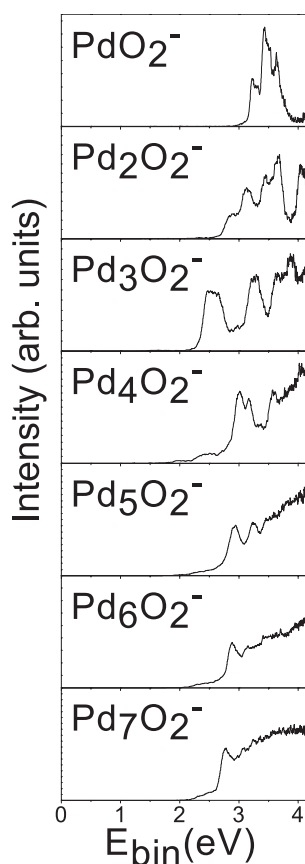


Fig. 3. UPS spectra of the Pd_nO_2^- ($n = 1-7$) clusters prepared using atomic oxygen method.

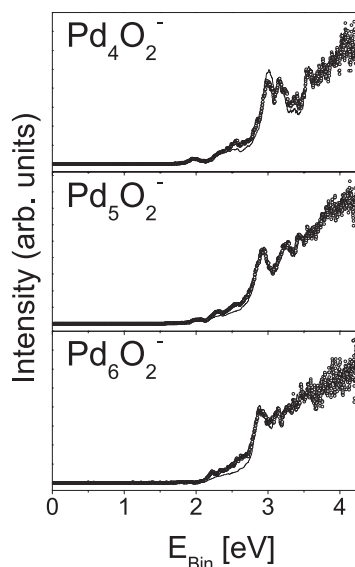


Fig. 4. UPS spectra of Pd_nO_2^- ($n = 4-6$) clusters prepared using the atomic and molecular oxygen methods. Dotted spectra are taken from the clusters prepared by the molecular oxygen method, whereas continuous curves by the atomic oxygen methods.

of these clusters, which can be observed by our UPS data. For PdO_2^- , the spectrum does not change depending on the preparation route (atomic or molecular oxygen methods). The spectrum agrees within an accuracy of 10 meV with the spectrum from Lineberger's group obtained with a photon energy of 3.406 eV [30]. As already discussed in reference [30], the O_2 molecule is dissociatively bound and the cluster has the linear geometry O-Pd-O. We could not find any evidence for the existence of a molecularly bound

complex in $\text{Pd}(\text{O}_2)^-$, which is expected to have a much lower electron affinity analogous to the case of NiO_2 [31].

For Pd_nO_2^- with $n = 2, 3$, no clear assignments of the chemisorption structures of oxygen can be provided (Fig. 3). The spectra do not show any detectable change depending on the synthesis method. A relatively high electron affinity of OPd_2O^- can be taken as an indication of dissociative chemisorption, even though no clear assignment on the chemisorption structure of oxygen can be made solely based on the experimental data shown here.

Figure 4 displays two spectra of each of the Pd_nO_2^- clusters with $n = 4-6$, one obtained by the reaction with atomic oxygen (line) and the other one obtained by the reaction with molecular oxygen (dotted). The main features of the UPS spectra do not change depending on the preparation methods. Small changes can be observed by using different cluster synthesis methods. Relative intensities of features in a spectrum change slightly depending on the preparation method. This might be related to the fact that some isomers of a cluster exist, changing their relative concentrations depending on the preparation method. However, different experimental conditions such as cluster temperatures may yield different UPS spectra of a cluster. Further studies are required to shed more light onto the problem of different isomers of Pd_nO_m^- clusters.

It is important to mention that the purity of the oxygen gas is high enough so that the entire features shown here can be assigned to the Pd_nO_2^- clusters rather than the hydroxide impurities. Our observation that the insertion of molecular oxygen results in the attachments of even numbers of oxygen atoms (corresponding to the integer numbers of oxygen molecules) should be an indication that our experimental data should be dominated by pure oxygen rather than other impurities. Also, the PdO_2^- result is in agreement with previous studies, confirming a high purity of the clusters studied here using UPS [28].

4 Summary

In conclusion, we found that Pd cluster anions consisting of up to 10 atoms can react with at most 2 oxygen molecules, and there is no pronounced size-dependent change of the oxygen chemisorption reactivity observed in the present work. We suggest that the oxygen chemisorption pattern is dominated by electronic properties of the clusters rather than specific adsorption sites. Using two different preparation methods of Pd cluster anions reacted with oxygen (atomic and molecular oxygen methods), no significant changes could be observed in the UPS spectra of a cluster, implying that activation barrier does not play a significant role for the chemisorption of oxygen molecules on Pd cluster anions in our experimental conditions.

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