Molecular Chemisorption of Oxygen on Cu_6 Cluster Anions

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Received: January 22, 2004; In Final Form: September 14, 2004

Using vibrationally resolved ultraviolet photoelectron spectroscopy, we demonstrate that O_2 molecularly adsorbs on Cu_6^- at room temperature. On Cu_6^-, we found that dissociation of O_2 is energetically feasible, but kinetically hindered. These results are unexpected on the basis of the previous observations that O_2 dissociatively chemisorbs on Cu bulk surfaces as well as Cu monomer and dimer anions, which can lead to the formation of Cu oxide. By changing the sizes of nanoclusters atom by atom, one can observe new chemical properties, which are not expected on the basis of the results from atom, diatomic molecule, and respective bulk materials consisting of the same element.

Interaction of oxygen with metals is one of the most fundamental problems in chemistry and physics. Adsorption and activation of oxygen molecules (O_2) are very important elementary steps in various heterogeneously catalyzed reactions. Moreover, by studying chemisorption of oxygen, one can obtain a better understanding of oxidation of metals, which is related to the corrosion process as well as electronic devices consisting of oxide materials.[1,2]

Materials consisting of few or few tens of atoms can exhibit properties that are much different from those of the bulk counterparts. Moreover, for these small clusters, every additional atom can drastically change electronic and geometric structures of a material. Interaction of oxygen with metals also changes significantly with the increasing number of atoms in a particle in this size regime.[3−9] Consequently, unusual chemical activities can be observed for nanoclusters, which are not observed on the corresponding bulk counterparts.[3−12] For example, even-numbered Au cluster anions smaller than Au_{21}^- generally react with O_2, whereas the odd numbered clusters are inert.[5−9] This even−odd alternation of the O_2 chemisorption reactivity can also be found for Ag cluster anions. The difference between Ag and Au is that O_2 chemisorption on Au cluster anions can be detected up to Ag_{40}^-, whereas Au cluster anions larger than Au_{21}^- do not react with O_2.[7,8] Using vibrationally resolved ultraviolet photoelectron spectroscopy (UPS), we found O_2 adsorbed molecularly on the even-numbered Ag and Au cluster anions, and the activated dioxygen species were suggested to be important reaction intermediates of various catalytic reactions such as low-temperature CO oxidation and partial oxidation of propylene.[7,8] These results are quite different from those of Ag and Au bulk crystals, on which oxygen dissociatively chemisorbs (Ag) or does not adsorb at all (Au).[13,14]

In the present work, we report the results for the O_2 chemisorption on Cu_6 and Cu_7 cluster anions. Cu has one electron in the 4s valence shell, and the valence electronic structure of Cu is quite similar to those of Ag and Au. However, previous studies have shown that the O_2 chemisorption pattern on Cu is quite different from those of Ag and Au. The aforementioned even−odd relationship of the O_2 chemisorption is much less pronounced on Cu cluster anions; i.e., not only even-numbered but also odd-numbered Cu cluster anions exhibit significantly high reactivities toward O_2 chemisorption.[9] The heat of the dissociative chemisorption of bulk surfaces corresponds to −326 kJ/ml for Cu, −62 kJ/mol for Ag, and +54 kJ/mol for Au, implying that the propensity of Cu toward dissociative chemisorption of O_2 is much stronger than on Ag and Au bulk surfaces.[15] Moreover, O_2 also dissociatively adsorbs on Cu monomer and dimer anions.[16−18] On the basis of the previous data for the Cu monomer, dimer and bulk crystals, it seems that O_2 chemisorbs dissociatively on Cu clusters independent of the cluster size.[9] In the present work, however, we provide evidence that O_2 molecularly adsorbs on Cu_6 cluster anions. The chemical properties of nanoclusters in a certain size range can differ considerably from those of the smaller molecules and bulk materials consisting of the same element.

To synthesize $Cu_nO_2^-$ (n = number of Cu atoms), Cu clusters were produced in the Pulsed Arc Cluster Ion Source (PACIS). After the Cu clusters were cooled to room temperature in the extender, they were exposed to O_2 (~0.1 mbar or less) (molecular oxygen method). Alternatively, O_2 was dissociated in the electric arc, and then reacted with metal atoms evaporated from the Cu electrode (atomic oxygen method). In this case, Cu and oxygen atoms pass the extender together, at which point the clusters form. Using the molecular oxygen method, it is possible that dissociative chemisorption does not take place, because the dissociation is thermodynamically more favorable, but kinetically hindered. In the atomic oxygen method, kinetic barriers for breaking the O−O bond do not play a role, and thus most likely the ultimate thermodynamic ground state in the chemisorption is reached. As shown in Figure 1, the molecular oxygen method yields only $Cu_nO_2^-$, whereas the atomic oxygen method allows formation of $Cu_nO_1^-$ and $Cu_nO_2^-$, indicative of efficient dissociation of O_2 in the gas phase before reacting with Cu clusters. In principle, we cannot rule out the possibility of the existence of small amounts of molecular oxygen in the atomic oxygen environment. However, it will be shown that UPS spectra of $Cu_6O_2^-$ synthesized using two different methods are completely dissimilar, indicating that concentration of molecular oxygen in the gas phase is negligibly small (Figure 2). The temperature of the clusters at the UPS measurement stage 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).

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10.1021/jp049674c CCC: $27.50 © 2004 American Chemical Society
Published on Web 11/12/2004

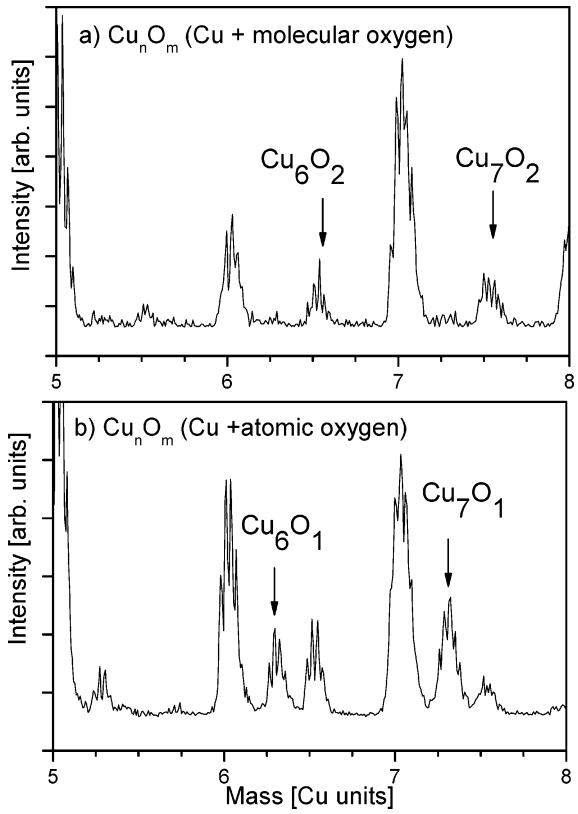

Figure 1. Mass spectra of Cu cluster anions exposed to oxygen atmosphere. Using the first method (a), only $Cu_nO_2^-$ can form, indicating that molecular oxygen reacts with Cu clusters in this case. In the second preparation method (b), one can find Cu_nO^- and $Cu_nO_2^-$, indicating that atomic oxygen formed in the gas-phase reacts with Cu. For more details about preparation methods, please see the text.

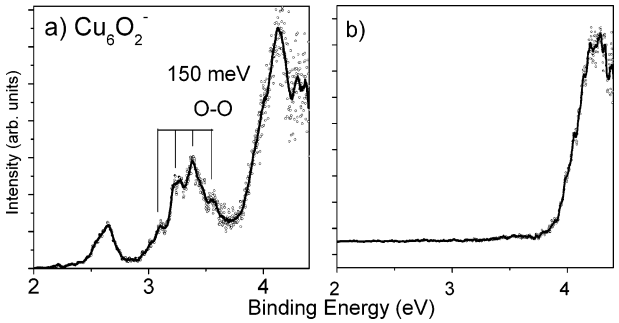

Figure 2. UPS spectra of $Cu_6O_2^-$. (a) Prepared using molecular oxygen environments. The vibrational fine structures correspond to 150 meV, which is assigned to the O−O stretching frequency of a superoxo-species. (b) Prepared using atomic oxygen method.

As shown in Figure 1, the mass resolution is high enough to resolve different isotopes of Cu. More detailed information on our experimental setup can be found in refs 19 and 20. The masses of the $Cu_{n-1}O_6$ and Cu_nO_2 clusters are separated by 1 atomic unit, and therefore, discrimination between these two different clusters using our mass spectrometer is difficult for larger clusters. However, it is important to note that Cu_n^- with $n = 6-12$ were shown to allow attachment of only one O_2 molecule in the previous studies of Ervin et al., and therefore, we rule out the possibility of the formation of $Cu_nO_6^-$ at the cluster size range of $n > 5$.[9] Our UPS spectra of CuO_2^- and $Cu_2O_2^-$ are consistent with previous ones from Wang et al., demonstrating a high reliability of our UPS spectra.[16−18]

Figure 2 shows the UPS spectra of $Cu_6O_2^-$, which were produced using atomic and molecular oxygen methods. $Cu_6O_2^-$ yields different UPS spectra depending on the preparation method. Using atomic oxygen instead of molecular oxygen, possible activation barriers for the dissociative chemisorption can be easily overcome, and ultimate ground states in the chemisorption can be reached. Observation of two different UPS spectra depending on the preparation method for $Cu_6O_2^-$ implies that oxygen chemisorbs nondissociatively using the molecular oxygen method, yet atomically using atomic oxygen environments; i.e., dissociative chemisorption of O_2 on Cu_6^- is energetically favorable, but kinetically hindered. A much higher electron affinity (the electron affinity is defined to be the energy difference between the ground state of a cluster anion and that of the corresponding neutral) of $Cu_6O_2^-$ prepared using atomic oxygen environments compared to that synthesized by the molecular oxygen method is also in line with this scenario, because the dissociative chemisorption of oxygen is expected to give a higher electron affinity than the molecular chemisorption. Note that the electron affinity of Cu_6O_2 prepared by molecular oxygen amounts to 2.2 eV, and the electron affinity is increased by 1.5 eV when atomic oxygen is used instead of molecular oxygen for the cluster synthesis (Figure 2).

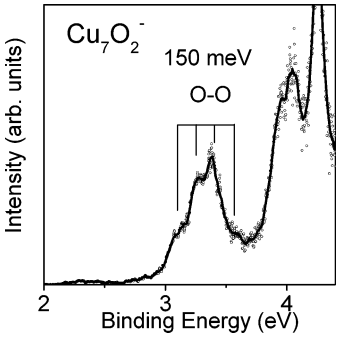

Figure 3. UPS spectrum of $Cu_7O_2.^-$

In the case of Cu_7^-, atomic and molecular oxygen methods result in the almost same UPS spectra of $Cu_7O_2^-$ (Figure 3). This result can be interpreted in two different ways: oxygen is either always atomically bound or molecularly chemisorbed, independent of the preparation method.

A close inspection of the UPS spectra allows us to discriminate some vibrational fine structures in the UPS spectra in Figure 2a, which can provide us information on chemisorption structures of oxygen on the Cu cluster anions. For $Cu_6O_2^-$, no vibrational fine structure is resolved in the first peak at about 2.6 eV; however, features between 3 and 3.6 eV contain several equally distanced subpeaks, which should correspond to the vibrational frequency of a Cu_6O_2 neutral cluster. The peaks at 2.6 and 3−3.6 eV are attributed to the transitions from the ground state of the anion to the ground and the first excited state of the neutral, respectively. The vibrational fine structures in an anion UPS spectrum correspond to the vibrational frequency of the neutral with the same geometry as that of the anion ground state. In principle, vibrational fine structures are expected to be present in both features; however, a low intensity of the first peak at 2.6 eV does not allow observation of vibrational progressions in this feature; i.e., we can only observe the vibrational frequency of the neutral Cu_6O_2 in the first excited state. Most likely, the ground and the excited state of the neutral differ by the spin multiplicity, which may not play a significant role for the O_2 chemisorption. Therefore, one can assume that the chemisorption geometries of Cu_6O_2 in the ground and the first excited state show a minor difference. The periodicity of the fine structure between 3 and 3.6 eV in Figure 3 amounts to about 150 meV, corresponding to the O−O stretching fre-

quency.[8] This should be evidence for the existence of the O−O bond in Cu_6O_2; i.e., O_2 does not dissociate on Cu_6^-.

For $Cu_7O_2^-$, a 150 meV periodicity can also be observed in the UPS spectrum (Figure 3), and therefore, we suggest molecular chemisorption of O_2. In this case, the vibrational fine structure is present in the first peak from the lowest binding energy, indicating that this fine structure corresponds to the vibration of the neutral Cu_7O_2 cluster in its ground state. It is important to mention that the features at the lowest binding energy range in Figures 2 and 3 should contain significantly high contributions from the antibonding $2\pi^*$ orbitals of O_2, and therefore, photoelectron detachments from these states should change the O−O bond length, yielding the vibrational progression of the O−O bonding. Determination of the vibrational frequencies based on our UPS spectrum may contain large error bars (about 20 meV) due to relatively high signal-to-noise ratios, and therefore, further theoretical studies on this subject will be required to shed light on the chemisorption structures of oxygen on the Cu cluster anions.

Our result indicates that at certain cluster sizes, Cu can become resistant toward oxide formation, because the dissociative chemisorption is the precursor state of the oxide formation.[21] Reactions of coinage metal cluster anions with oxygen can be explained within an electronic model, in which lower binding energies of valence electrons facilitate metal to oxygen charge transfers, yielding larger reactivities toward oxygen chemisorption.[5−9] That Cu_6^- and Cu_7^- do not allow dissociation of the O−O bonding can be rationalized by relatively high electron affinities of these clusters, which hamper metal to oxygen charge transfers, thus causing the molecular chemisorption.[22] In particular, Cu_7^- has a closed electronic shell configurations, having a high electron affinity of the neutral counterpart and a large gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the anionic cluster, which might reconcile the chemical inertness of this cluster.[22] However, these results are surprising, considering that the electron affinities of Cu_6 and Cu_7 are much lower than those of other larger Cu clusters, which should dissociate O_2, forming Cu oxide.[23,24] It is interesting to note that the reactivities of Cu_6^- and Cu_7^- toward O_2 chemisorption are much lower than those of Cu_n^- with $n = 1-4$, because these smaller clusters can react with more than two O_2 molecules, whereas Cu_6^- and Cu_7^- allow attachment of only one O_2 molecule on a cluster. Our result that Cu_6^- and Cu_7^- do not allow dissociation of O−O bonding can reconcile the reactivity data in ref 9.

Chemisorption properties of O_2 on Cu_6^- and Cu_7^- seem to be analogous to those of Au cluster anions in the range of 2−12 atoms, because the molecular chemisorption of oxygen was also observed for the even-numbered Au cluster anions.[9] For even-numbered Au cluster anions reacted with O_2, the UPS spectra showed vibrational fine structures of O−O stretching frequencies, and the activated diatomic oxygen species were suggested to be important reaction intermediates.[4,6,8] On the basis of our results in the present work, it is suggestive that Cu clusters with certain sizes may be promising candidates for catalyzing those reactions, for which formation of activated dioxygen species are important (such as low-temperature CO oxidation and propylene epoxidation).

In summary, we have demonstrated that O_2 molecularly adsorbs on Cu_6^- and Cu_7^-. For Cu_6^-, O_2 dissociation is energetically favorable but kinetically hindered. For Cu_7^--, the nondissociative chemisorption of O_2 seems to be energetically more favorable than dissociative chemisorption. The results from Cu_6^- and Cu_7^- are much different from the chemisorption properties of O_2 on Cu bulk surfaces as well as Cu monomer and dimer anions, which efficiently dissociate O_2, forming Cu oxides. By changing the size of nanoclusters atom by atom, one observes new chemical properties with respect to those of the atom, diatomic molecule, and respective bulk materials consisting of the same element.

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

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