

Sequential Oxygen Atom Chemisorption on Surfaces of Small Iron Clusters

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We report photoelectron spectra of iron oxide clusters, Fe_xO_y^- ($x = 1-4$, $y = 1-6$). For a given x , we find that the electron affinity increases with the number of O atoms, consistent with an increasing degree of oxidation. The results are interpreted based on charge transfer interactions between the Fe_x clusters and the O atoms, and provide key information about the oxide cluster structures, in which each O atom is suggested to locate on the surface of the clusters for the $x = 3$ and 4 series. These clusters provide novel model systems to understand the electronic structure of bulk iron oxides. [S0031-9007(96)00370-5]

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The interaction between iron and oxygen is one of the most important chemical processes in understanding corrosion, biological oxygen transport, and oxide film formation. Even though there have been extensive studies on the oxidation of single crystal iron surfaces [1-3] and elementary studies on the reaction between iron and oxygen [4,5], a complete understanding about the interaction of oxygen with iron and the iron oxide surfaces is still lacking. Well-controlled studies on small iron oxide clusters not only provide a new avenue to obtain detailed information about the interaction between oxygen and iron but also provide models for the iron oxide materials [6] and iron oxide surfaces [7,8].

Bulk iron oxides have several different forms ranging from FeO and Fe_3O_4 (magnetite) to Fe_2O_3 (hematite), each with interesting properties. Their electronic structures have been the subjects of many investigations [9-11]. Generally, these compounds are viewed as charge transfer oxides with strong ionic interactions between the iron and oxygen atoms. From FeO to Fe_2O_3 , the oxidation state of the Fe atom is increased from +2 to +3 while Fe_3O_4 is a mixed valency compound containing Fe atoms with both +2 and +3 oxidation states. All three oxide phases can be formed during oxidation of iron surfaces from FeO to Fe_2O_3 with increasing oxygen exposure and substrate temperature [1].

In this Letter, we report the first study of a series of small iron oxide clusters, Fe_xO_y^- ($x = 1-4$, $y = 1-6$), using size-selected anion photoelectron spectroscopy. We find that, in general, the electron affinity (EA) of the oxide clusters with a given number of iron atoms increases with the number of oxygen atoms, consistent with an increasing degree of oxidation. Interestingly, for $x = 3$ and 4, the EA of the oxide clusters increases linearly with the number of O atoms after the first oxygen atom adsorption. The results are interpreted by an electrostatic model, in which a charge transfer occurs from the iron cluster to the O atoms. This leads to a series of structures in which the oxygen atom is suggested to be sequentially added to the cluster surfaces. These results imply that for the Fe_3O_y and

Fe_4O_y clusters there is significant metal-metal bonding even for clusters with an Fe:O ratio comparable to the bulk stoichiometry. The oxide clusters appear to exhibit unique bonding characteristics compared to the bulk iron oxides, where there is no direct metal-metal bonding.

The experiments are performed with a photoelectron spectroscopy apparatus that has been described in detail elsewhere [12]. It couples a laser vaporization cluster source with an improved magnetic bottle time-of-flight (TOF) photoelectron analyzer [13]. An intense pulsed laser beam is focused onto a pure iron target, producing a plasma containing iron atoms in both charged and neutral states. A pulsed helium carrier gas containing 0.1% O_2 is mixed with the plasma. The reactions between the iron atoms and the oxygen produce the desired Fe_xO_y^- clusters. The helium carrier gas and the oxide clusters undergo a supersonic expansion, forming a cold molecular beam. The clusters of interest are mass selected and decelerated before photodetachment by a pulsed laser beam (355 or 266 nm). The apparatus has a resolution of better than 30 meV at 1 eV electron energy. The electron kinetic energy distributions are calibrated with the known spectrum of the Cu^- anion and are subtracted from the photon energies to obtain the presented electron binding energy spectra.

We focus on clusters with a fixed number of Fe atoms and various O atoms. These are clusters with an increasing degree of oxidation and unusual stoichiometry. The oxide cluster distribution can be slightly varied by the O_2 content in the carrier gas with a lower O_2 content favoring more oxygen-deficient Fe_xO_y^- clusters. The distribution also depends on the resident time inside the nozzle. Longer resident time, i.e., a longer reaction time, favors clusters with high oxygen content. For the four cluster series reported here, the highest oxygen content cluster observed for each series is, Fe_2O_6^- , Fe_3O_6^- , Fe_3O_8^- , and $\text{Fe}_4\text{O}_{10}^-$, respectively. However, as will be shown below, some of the high oxygen content clusters have EAs that are too high for them to be studied at the current photon energies (3.49 and 4.66 eV). The highest oxygen content cluster that we are

able to study for each series is FeO_4^- , Fe_2O_5^- , Fe_3O_5^- , and Fe_4O_6^- , respectively.

Our main results are summarized in Fig. 1 that shows the photoelectron spectra for FeO_y^- ($y=1-4$), Fe_2O_y^- ($y=1-5$), Fe_3O_y^- ($y=1-5$), and Fe_4O_y^- ($y=1-6$) at 4.66 eV photon energy (266 nm). These spectra represent transitions from the ground state of the anions to the various states of the neutral species and can be viewed as the electronic excitation spectra of the neutral clusters. The detachment thresholds represent the EAs of the neutral clusters. For spectra with resolved vibrational structures, the EA can be determined fairly accurately. However, broad spectra are often observed, and the EAs are estimated by drawing a straight line at the leading

edge of the spectra and adding a constant of 0.05–0.07 eV to the intercept with the binding energy axis. The constant is added to account for the instrumental resolution and thermal broadening. Well-resolved spectra are observed for the FeO_y^- and Fe_2O_y^- clusters with vibrational structures resolved for several species. The Fe_3O_y^- and Fe_4O_y^- spectra become increasingly more complicated, and discrete electronic features are more difficult to resolve. We also performed experiments at 3.49 eV photon energy (355 nm) and obtained slightly better resolved spectra. For the Fe_3O_y^- and Fe_4O_y^- series, qualitatively the same spectra are observed, except for Fe_4O^- for which the shoulder near the detachment threshold is resolved into a well-defined peak at the lower photon energy. For certain clusters, long tails are observed at the lower binding energy side. These are seen more clearly in the spectra of Fe_3O_5^- and Fe_4O_6^- and are most likely due to hot band transitions and population of other minor isomers with low EAs. The tiny feature at the low energy side of the Fe_4O_2^- and Fe_4O_5^- spectra may be due to the latter. These weak features always depend on the source conditions.

The most interesting observation is the EA increase as a function of the number of O atoms in each cluster series, except for Fe_2O_2 in the Fe_2O_y series. These are plotted in Fig. 2 along with the EA values of the pure Fe_x clusters [12,14]. For the FeO_y series, the EA increase is saturated at FeO_3 and there is no increase from FeO_3 to FeO_4 . For the Fe_2O_y series, the EA increase is smaller from Fe_2O_4 to Fe_2O_5 and appears to approach a saturation. For both the Fe_3O_y and Fe_4O_y series, the first O atom addition does not produce an EA increase, and nearly linear increases are observed after that. From Fe_3O_4 to Fe_3O_5 , there is a large EA increase, and Fe_3O_6 and higher clusters have EA values that are too high to be studied at the current detachment energy (266 nm). The same is observed for the Fe_4O_y series, where Fe_4O_7 has an EA value larger than 4.2 eV, representing a significant jump from Fe_4O_6^- . The higher clusters all have larger EAs and cannot be studied at 266 nm.

The spectra shown in Fig. 1 represent the electronic structures of these oxide clusters. However, detailed assignments of these spectra will require accurate *ab initio* calculations. Except for the FeO diatomic molecule [15], no such calculations are yet available. In particular, the FeO_y and Fe_2O_y series represent novel gas phase molecular species and will be dealt with in detail separately [16]. In the remainder of this paper, we will focus on the Fe_3O_y and Fe_4O_y series where a linear dependence of EA vs O is observed for a range of O atoms. A simple electrostatic model is used to interpret the linear trend. This simple consideration, together with the previous works on the structures of the pure clusters [17] and single O-adsorbed clusters (Fe_xO) [18], leads to interesting suggestions for the structures of these oxide clusters and insight into their unique bonding characteristics.

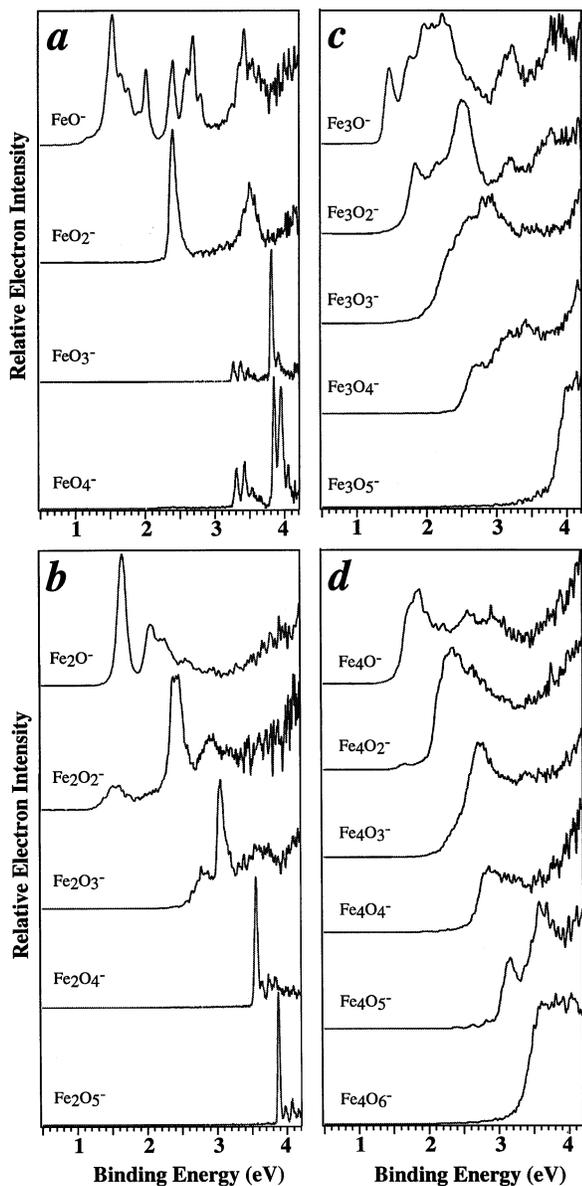


FIG. 1. Photoelectron spectra of Fe_xO_y^- clusters taken at 4.66 eV (266 nm) photon energy. (a) FeO_y^- ($y=1-4$), (b) Fe_2O_y^- ($y=1-5$), (c) Fe_3O_y^- ($y=1-5$), (d) Fe_4O_y^- ($y=1-6$).

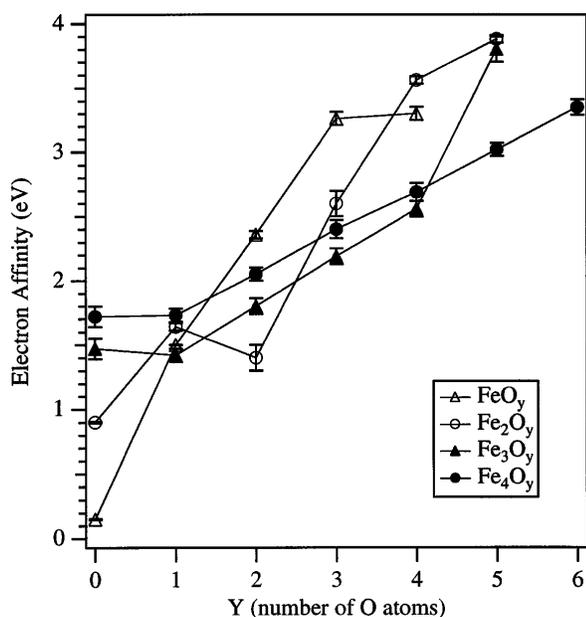


FIG. 2. The electron affinity of the Fe_xO_y clusters versus the number of O atoms. The values for Fe and Fe_2 are from Ref. [14], and that for Fe_3 and Fe_4 from Ref. [12].

The general trend of the EA increase with the number of O atoms is consistent with the increasing degree of oxidation. As is well known in the bulk oxides [9], the interactions between the Fe atoms and the O atoms in the Fe_3O_y and Fe_4O_y clusters are expected to be predominantly ionic. The linear dependence of the EA on the number of O atoms in the Fe_3O_y ($y = 1-4$) and Fe_4O_y ($y = 1-6$) clusters can be understood based on a simple electrostatic model, if we assume that each oxygen atom is located on the cluster surface with a net charge transfer, δe , from the Fe_x iron cluster to each adsorbed O atom, i.e., $(\text{Fe}_x)^{y\delta+}(\text{O}^{\delta-})_y$. The EA, by definition here, is the energy required to remove the extra electron from the Fe_xO_y^- clusters. The EA is approximately proportional to two terms: (1) the electrostatic repulsion of the extra electron with the $\text{O}^{\delta-}$ atoms, $-y\delta e^2/R$, where R is the average distance between the extra electron and the $\text{O}^{\delta-}$ atoms; and (2) the electrostatic attraction between the electron and the positively charged metal center, $y\delta e^2/r$, where $y\delta e$ is the total charge on the metal center and r is the average distance between the electron and the positive charge center. On the basis of this simple electrostatic model, the EA should be proportional to y , the number of O atoms, with a slope of $\delta e^2(1/r - 1/R)$.

This simple electrostatic consideration seems to be able to account for the linear portions of the EA vs y curves for Fe_3O_y and Fe_4O_y (Fig. 2) remarkably well. The underlying assumptions in this model are that the charge transfer (δe) to the O atom is the same at each step of oxidation and that the O atoms are located on the cluster surface around the metal core. However, the first O oxidation step does not produce an increase in the EA and seems to be inconsistent with the model. The same

phenomenon has been observed with larger Fe_x clusters as well, where the first O adsorption even induces a decrease of EA for $x = 8-15$ [18]. For all other transition metal clusters we have studied (Ti, V, Cr, Co, and Ni), we have observed the similar phenomenon: For the trimer and tetramer, the first oxidation does not induce an increase of EA [19]. However, there is no reason to believe that the first oxidation is less ionic than the subsequent oxidation. One plausible interpretation is that, for the Fe_3O^- and Fe_4O^- clusters, the electrostatic repulsion and attraction experienced by the extra electron cancel each other out. This would suggest that upon further oxidation the negative charges on the O atoms are screened and that, on average, the extra electron experiences more attraction than repulsion for the higher clusters, giving rise to the linear increase with y .

It is interesting to speculate about the possible structures of these oxide clusters on the basis of the experimental observations and the electrostatic model. The iron trimer is known to have an equal triangular D_{3h} structure while the tetramer has a tetrahedral T_d structure [17]. Our previous study on single O atom adsorption on small iron clusters found that the O atom prefers the edge site, bridging two iron atoms for the dimer, trimer, and tetramer, with the face sites more favored as the iron clusters become larger [18]. Studies on the O-atom adsorption on small Ni clusters also found that the O atom prefers the edge site on the tetrahedral Ni_4 cluster [20]. A recent study on Nb_3O finds a similar structure with the O atom bridge bonded to two Nb atoms [21]. The bridge site adsorption in these small transition metal clusters is surprising because it is known that on bulk surfaces the fourfold sites are usually favored [1]. This is probably due to the more compact structures of the small clusters, which optimize the O $2p$ bonding to the metal atoms in the bridge sites. Therefore, it is reasonable to assume that for the higher oxide clusters the O atoms will occupy the bridge sites successively. The oxide cluster structures consistent with this picture are depicted schematically in Fig. 3.

These series of clusters are quite interesting because they cover the whole range of stoichiometries found in the bulk oxides. If we assume that the O atom has an oxidation state of -2 , then the oxidation states of the Fe atoms can be evaluated in each cluster, depending on the O atoms a given Fe atom is bonded to. Therefore, we find that in both Fe_3O_3 and Fe_4O_4 the Fe atoms have $+2$ oxidation state, and they may be viewed as fragments of the bulk FeO oxide. In Fe_3O_4 , if the fourth O atom is bridge bonded to two Fe atoms, we then find that there are two Fe atoms with $+3$ and one with $+2$ oxidation state, similar to the bulk magnetite (Fe_3O_4). Finally, in Fe_4O_6 , each Fe atom reaches the high oxidation state of $+3$, similar to bulk hematite. For the clusters with an O:Fe ratio less than 1, they may be compared to the initial oxidation of Fe surfaces, although the fourfold sites that O atoms prefer on the bulk surfaces are not available in these small clusters. It is also important to point out that, for

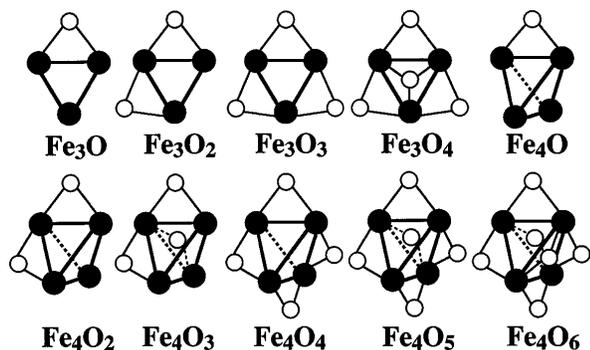


FIG. 3. Schematics of the proposed structures for the Fe_3O_y and Fe_4O_y oxide clusters. The structures for Fe_3O and Fe_4O are from Ref. [18].

both Fe_3O_4 and Fe_4O_6 clusters, one more O atom addition would make at least one Fe atom to have an oxidation state beyond the normal +3. This may explain the EA jump in both cases.

All these structures are highly idealized and are suggested based on the sequential O atom adsorption on the cluster surfaces occupying the Fe-Fe bridge sites. This, in turn, is based on the electrostatic interactions between the Fe and O atoms, used to interpret the linear EA curves shown in Fig. 2 for Fe_3O_y ($y = 1-4$) and Fe_4O_y ($y = 1-6$). Final determination of the cluster structures will require accurate *ab initio* calculations and comparison between the calculations and the experiments. Interestingly, all the structures suggested in Fig. 3 have substantial Fe-Fe interactions, even in the clusters with similar stoichiometry as in the bulk, i.e., $(\text{FeO})_n$ ($n = 3$ and 4), Fe_3O_4 , and $(\text{Fe}_2\text{O}_3)_2$. These clusters may be too small to model bulk properties, but they may provide interesting insight about the nature of the bonding and magnetic properties of the bulk materials. All the structures shown in Fig. 3 appear to optimize the Fe-O bonding and allow Fe-Fe metallic bonding at the same time. This may be a major difference between the finite systems and the bulk, where the metal atoms are well separated and cannot have direct metal-metal bonding. Preliminary density functional theory calculations indicate that these structures are indeed highly favored [18,22].

In conclusion, we report the photoelectron spectra of small iron oxide clusters with various stoichiometries. The small Fe_xO_y clusters can be viewed as sequential oxygen atom adsorption to the surfaces of the Fe_x ($x = 3, 4$) clusters, leading to nearly linear increase of the EA with y . This is interpreted by a simple electrostatic model involving a net charge transfer from the Fe_x cluster to the O atoms. These results provide important electronic structure information for the small iron oxide clusters. They can be directly compared with rigorous quantum calculations, which may also be able to address the question of the magnetic properties of these clusters and how they vary with the different degree of oxidation and aggregation. These experiments also demonstrate the flexibility of the cluster beam technique to synthesize oxide clusters with unusual

stoichiometries, which may be important to understand the formation of oxide films and the initial nucleation.

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- [22] Preliminary DFT calculations similar to those done in Ref. [18] are performed for Fe_3O_y ($y = 1-4$) and Fe_4O_y ($y = 1-6$). The calculations indicate that for all these oxide clusters the O atoms prefer to bridge bond to two Fe atoms [L. Lou (private communication)].