Dual Reactivity of Iron Oxide Clusters: Self-Stimulated CO Oxidation As Well As NO Reduction

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The worldwide demand for a reduction in global warming and the current environment problems associated with acid rain, stratospheric ozone, and greenhouse gases¹ require a reduction in combustion products such as CO and NO. While undesirable, these gases are some of the chemical components in automobile exhausts, cigarette smoke, and other industrial processes including the production of hydrogen fuel cells². Thus a search is under way to find catalysts/reactants that could simultaneously eliminate both gases. This is a complex task since CO is a strongly bound molecule that can be eliminated by oxidation while NO is a relatively weakly bonded molecule whose elimination entails reduction. The challenge is then to find a reactant/catalyst that could simultaneously perform the dual role of oxidation and reduction. A step in this direction is to reduce NO via oxidation of CO. This can be accomplished³⁴, for example, by Pd particles or monolayers supported on MgO. While encouraging, such a solution lacks viable applications since the CO and NO are generally produced in widely different amounts. The need for a reactant that could perform these tasks individually and simultaneously is thus pressing.

In this report we show that the neutral iron oxide clusters can accomplish the dual task. Our studies of neutral iron oxide clusters interacting with NO and CO separately and together show that they generate CO₂ and N₂. Following the passage of iron oxide clusters
through a gas phase reaction cell with ca. $10^{-3}$ torr of CO or NO gas, the cluster and cluster complexes are ionized by an ArF excimer laser for detection of all species in the beam. We demonstrate that small Fe$_m$O$_n$ ($m=2, 3$, $n=1,2,3$) clusters accomplish the dual task through self-activated processes in which the adsorption of the first molecule creates conditions that stimulate the oxidation/reduction of subsequent molecules. The reason that the same cluster can oxidize as well as reduce lies in the fact that the oxidized clusters can accommodate a wider metal-oxygen ratio than in the corresponding bulk.$^5$. Consequently, at intermediate concentrations of oxygen, the same cluster has the potential to gain as well as donate oxygen. What is even more interesting is that the finite size facilitates these processes via two independent mechanisms. First, the reduced size allows structural rearrangements that diminish the reaction barriers. Second, the heat of adsorption of an initial molecule provides the energy needed to overcome the reaction barriers thus opening pathways for the reaction to occur. In real applications, the clusters need to be supported or stored in matrices. It is therefore important that the observed processes occur on neutral clusters.

Iron oxide clusters are generated$^{5-7}$ in beams via a supersonic pulsed nozzle shown in Fig.1. An ablation laser (532 nm @ 10Hz, doubled Nd/YAG output) with an energy/pulse of typically 5 mJ is focused to ~ 0.1 mm on the surface of a rotating drum to which is glued an iron foil. The ablation laser creates a plume of iron vapor (Fe, Fe$^+$, Fe$^-$, Fe$_m$, Fe$_m^+$, and Fe$_m^-$) which evolves into a gas pulse of expansion gas from the nozzle. An expansion gas consisting of 0.75%O$_2$/He mixture provides the oxidant and stabilizer background to generate a neutral, stable cluster distribution of iron oxide clusters. Following the reaction of Fe$_m$ species with O$_2$, the iron oxide clusters are entrained in the gas pulse and expanded through a gas channel (2 mm x 25 mm) into the vacuum chamber held at ~ $5 \times 10^{-6}$ Torr during the
ablation process. The resultant cluster beam, as it expands from the ablation nozzle, is first subjected to an electric field, generated by applying 600V between the deflection plates, to remove any ions generated in the process. It is important to underscore that the removal of ions ensures that the observed chemistry is due entirely to the neutral clusters.\textsuperscript{5,6}

The neutral beam then enters the reaction cell consisting of a skimmer at the entrance and a hole at the exit. The input and output holes are 2 mm in diameter and the cell is ~ 6 cm in length including the skimmer. Reaction gas (in this instance, CO, NO or both) is introduced into the cell: consequently, the clusters pass through the cell and collide with the reaction gas.

Upon exiting the reaction chamber, the clusters pass into the ionization region (ion source region) of a time of flight mass spectrometer (TOFMS) for detection. The neutral clusters are ionized via an excimer ArF laser (193nm). The cluster ions accelerated by the TOFMS are directed into a dual microchannel plate detector (MCP) at the end of a 1.5 m flight. The TOF mass signals are monitored by a Galileo microchannel plate detector.

Figure 2 shows the mass spectra of the neutral Fe\textsubscript{n}O\textsubscript{m} clusters and the change in the mass distribution as these clusters pass through a reaction cell with various pressures of CO. Spectra 2 (a) and (d) represent the cluster distribution for non-reacted clusters in the different mass regions. Spectra 2(b) and (c) present the intensities of Fe\textsubscript{m}O\textsubscript{n} clusters for the reacted species under different pressures of CO. Selected clusters are identified via their composition numbers (n,m). Spectra 2 (e) and (f) present the concentration of C, O, CO and CO\textsubscript{2} for various pressures of CO in the lower mass region. Spectra 2 (a) - (c) focus on the Fe\textsubscript{m}O\textsubscript{n} clusters and indicate that the clusters Fe\textsubscript{2}O\textsubscript{1,2} and Fe\textsubscript{3}O\textsubscript{3} are special. These clusters undergo a dramatic relative reduction in concentration as CO is introduced into the reaction cell. In fact,
even at a CO pressure of $21 \times 10^{-4}$ torr, Fe$_2$O$_{1,2}$ clusters virtually disappear. Fe$_3$O$_3$ also experiences a dramatic reduction in intensity. On the other hand, larger clusters seem to survive even under the higher CO pressure. What is exciting is that the decrease in intensity of these clusters is concomitant with an increase in intensity of the CO$_2$ broad signal component as seen in spectra 2 (d)-(f). Combined, the observations demonstrate that these clusters are oxidizing CO to produce CO$_2$. Can the clusters that oxidize CO also reduce NO?

To explore this complementary possibility, the oxide clusters are exposed to NO. The results are presented in Fig. 3. Fig. 3(a) -(e) show the bare clusters and the clusters exposed to 16.5 and $21 \times 10^{-4}$ torr of NO in the high mass region. Figs. 3 (f)-(j) show the mass spectra of the bare and exposed clusters in the low mass region. The oxygen deficient species Fe$_2$O, Fe$_2$O$_2$, and Fe$_3$O$_3$ disappear as the NO concentration increases. The mass spectrum in the low mass region shows the appearance of N$_2$ implying that NO is being reduced in the reaction/ionization process. Note the presence of a small amount of N atoms in the reaction products. We will come to this point later. Product species CO$_2$ and N$_2$ have broad mass peaks due to their fragmentation from the Fe$_{m}$O$_{n}$ clusters upon ionization.

While the oxidation/reduction by the same cluster presents an exciting possibility, it does raise several issues. (1) How does the same cluster act to oxidize and reduce? (2) Why is it that the oxidation/reduction occurs readily for clusters of small sizes? (3) What is the microscopic mechanism? And, in particular, (4) What are the reaction barriers for these cluster supported reactions and how are they overcome so readily? To investigate these and other pertinent issues, we carried out first principles electronic structure investigations using state of the art density functional methods adapted to studies of small clusters. The actual investigations employed the DMOL set of codes. In this implementation, the cluster
electronic wave-functions are expressed as an anti-symmetrized product of molecular orbitals that are linear combinations of atomic orbitals situated at the atomic sites. Instead of using the Gaussian/Slater basis functions to express the atomic orbitals, the DMOL implementation uses a radial mesh to store wavefunctions in a numerical form. Matrix elements of the cluster hamiltonian required in a self consistent solution of the density functional equations are computed by numerically integrating over a logarithmic mesh of points. To provide variational freedom needed to describe changes in the wavefunction in the valence region, polarization functions are added to the atomic basis. The current work employs double numerical basis with 4p polarization functions for Fe and 3d polarization functions for O, N, and C. The gradient corrected functional proposed by Perdew et al.\textsuperscript{10} (BPW91) is used to incorporate exchange-correlation effects.

The ground state geometries of the pure Fe\textsubscript{m}O\textsubscript{n} (m=1-3, n=1,2) clusters are described in our previous publications\textsuperscript{11}. Notably, Fe\textsubscript{2}O\textsubscript{2} is a planar structure with no Fe-Fe bonds. For Fe\textsubscript{3}O\textsubscript{3}, the ground state is a ring-like structure with oxygen atoms mediating the Fe-triad. The focus of the current work is oxidation/reduction and, here, we shall focus only on Fe\textsubscript{2}O to elucidate the reaction mechanism.

Fig. 4 shows the reaction mechanism for the adsorption of CO and the corresponding energetics. In these studies, the CO molecules are brought toward the cluster along various initial trajectories to search for the ground state configuration. For each case, the energy is minimized by moving atoms along the directions of force until the forces drop below a threshold value. The first CO molecule can attach to a Fe site or form a CO\textsubscript{2} by coming towards an O atom. A study of the energetics shows that the attachment to Fe is more favorable by 1.75 eV. The CO binds to Fe with an energy of 1.93 eV which lowers the total
energy of the system as shown in Fig. 4. Another CO approaching the adsorbed cluster also prefers to bind to an Fe site compared to the O site by 1.92 eV. The additional binding energy to the Fe site is 1.86 eV and this further lowers the total energy of the system to 3.79 eV resulting in an Fe$_2$O cluster with two adsorbed CO's at the Fe sites. The key is to realize that the heat of adsorption provides enough energy to the system Fe$_2$O$_1$(CO)$_2$ such that the CO molecules undergo significant stretching. In fact, there is enough energy in the system to drive the cluster to a configuration in which the CO bond of one of the CO's is completely broken resulting in a rhombic Fe$_2$OC with opposing Fe corner sites each holding an additional CO molecule and an O atom. Of course, such a possibility requires overcoming the barriers. What is more interesting is that the heat of adsorption provides enough energy to stretch CO molecules. Note too that those clusters could be at a temperature near 700 K$^{12}$ and additionally extra energy can be added to the clusters in the ionization process.$^{5-7}$ Quite unexpectedly, the theoretical studies further show that if one of the CO's is stretched by 15%, an approaching CO molecule will combine with the O of this CO to form CO$_2$. To examine such a reaction, we started with a CO-Fe-O-Fe-CO cluster shown in Fig. 4 with one of the CO's stretched to 1.35 Å. Such a process required 1.67 eV of energy. A CO molecule is brought to a distance of 4.525 Å from the Fe site and the system is allowed to relax. Surprisingly, the approaching CO grabbed the stretched O to form CO$_2$. What is even more surprising is that once the CO is initially stretched, the CO$_2$ formation proceeds in a barrierless manner. Note that such a process results in the formation of C. Note also that C atoms are observed in the mass spectrum at lower masses.

A marginally different process also occurs for the NO reduction. The theoretical studies show that the ground state for the Fe$_2$O-NO cluster is a Fe$_2$ON rhombus with an O
atom bound to one of the Fe sites. Although we did not investigate the barrier for the
dissociation of the approaching NO, the NO binding energy is 3.14 eV. The heat of
adsorption, in our view, provides enough energy to overcome the dissociation of the
approaching NO. A second NO approaches the cluster either toward the N side or the Fe
site. Detailed study of the various paths and the energetics shows that the most stable
configuration corresponds to the NO approaching the N atom and forming N$_2$. In the process,
the O atom left by the approaching NO bonds with the two Fe sites resulting in a Fe$_2$O$_2$
rhombus and a loosely bound O and N$_2$. Note that the heat of adsorption could provide
enough energy to detach N$_2$ from the resulting cluster. Experimentally we observe both N$_2^+$
and CO$_2^+$ with broad mass spectral peaks indicating that they are fragmented from the
clusters on which they are generated during the ionization process. Absorption of 193 nm
photons during the ionization process can also contribute to the energy needed to induce the
reaction. They must leave the Fe$_2$O(CO)$_2$ and Fe2O(NO)$_2$ clusters as ions and the residual
cluster fragments (e.g., Fe$_2$O(O)$_2$ and Fe$_2$OC) must be neutral and undetected.

To summarize, we have shown that an Fe$_2$O cluster can oxidize a CO and reduce a
NO molecule via two different mechanisms. In the process, however, the cluster transforms
into a Fe$_2$OC or a Fe$_2$O$_3$ cluster. Our studies indicate a similar sequence of events for Fe$_2$O$_2$
to oxidize CO and reduce NO. The reason for this remarkable ability of small Fe$_m$O$_n$ clusters
to both oxidize and reduce lies in the fact that in small sizes the clusters are stable over a
wide range of compositions. Further, many of the reactions are barrierless because the cluster
geometry adapts to the changing environment. One should exert caution in noting that the
clusters themselves are transformed during the reaction. The above processes cannot,
therefore, be strictly classified as catalysis; however, numerous industrial processes do not
require reactions sustainable over long periods and thus, these clusters may be ideal for such applications. Moreover, catalytical processes involving bulk or condensed phase Fe$_2$O$_3$ with CO and NO almost always occur in the presence of other species, such as NO$_x$, O$_2$, H$_2$O, etc. The experimental mass spectra, do indicate something rather startling. The mass spectra in the low mass region shown in Figs. 2 and 3 do exhibit small peaks at C and N atomic masses respectively. This suggests that the C left behind in the oxidation of CO somehow can be removed from the cluster. While we don't fully comprehend the mechanism for this observation, it might offer hope that the clusters may continue to oxidize CO several times. We are in the process of investigating these observations. In the meantime, the dual oxidation/reduction, in our view, does offer an exciting area of research.

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References


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FIGURE CAPTIONS

Figure 1: Schematic drawing of the laser ablation nozzle, electric field ion deflector, reaction cell, and TOFMS ionization region. This apparatus is enclosed in a vacuum chamber with two 6” diffusion pumps evacuating the chamber and flight tube.

Figure 2: TOF mass spectra of iron oxide cluster in the region of (a)-(c) 100-600 and (d)-(f) 0-100 m/z as function of CO pressure in reaction cell. Spectra are observed by 193 nm ionization with 0.75 % O2/He expansion gas. Numbers (10^-4 Torr) at right side of trace indicate pressure in reaction cell. Note that in trace (a), signal intensities for clusters (2,1) and (2,2) are as large as those for (5,5) and (6,6) and (3,3) is the most intense feature in the mass spectrum. In traces (b) and (c), (2,1) and (2,2) rigid are missing and (3,3) intensity is now the smallest of all remaining features. The reduction of the absolute signal intensity with increasing pressure in the reaction cell follows that found for non reactive scattering (e.g., N2, Ar, CO2,…). The N2 and CO2 sharp features are background signals due to out gassing of the chamber. As the CO pressure increases in the cell, the amount of CO and CO2 (broad features) increases compared with sharp features of N2 and CO2. These broad features are caused by fragmentation of the Fe_mO_n (CO)_x clusters upon ionization. A C atom signal is also found in the mass spectrum that increases with high CO pressure in the cell.
Absolute intensities between traces cannot be compared: only relative intensities of features within each trace are meaningful.

Figure 3  TOF mass spectra of iron oxide clusters in the region of (a)-(e) 100-600 and (f)-(j) 0-100 m/z as function of NO pressure in reaction cell. Spectra are observed by 193 nm ionization with 0.75% O$_2$/He expansion gas. Numbers (10$^{-4}$ Torr) at right side of trace indicate pressure in reaction cell. The broad mass features N, NO, and N$_2$ are due to fragmentation of Fe$_m$O$_n$(NO)$_x$ upon ionization. N$_2$ signal exists without introducing NO into reaction cell, and is due to residual outgassing in the chamber. The broad features of N$_2$ and NO appear with high pressure of NO in the cell.

Fig. 4.  The ground state geometries of various CO adsorbed Fe$_2$O clusters marking the oxidation of CO. The energies of the various reaction processes are also shown. All energies are in eV.
Relative Binding Energy (eV)

- \( E = -1.93 \text{ eV} \)
- \( E = -1.86 \text{ eV} \)
- \( E = -0.63 \text{ eV} \)
- \( E = +1.67 \text{ eV} \)

13