

Self-Stimulated NO Reduction and CO Oxidation by Iron Oxide Clusters

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It is shown that a bare Fe_2O_3 cluster can oxidize CO to form CO_2 and reduce NO to form N_2 by undergoing compositional changes between Fe_2O_2 and Fe_2O_3 states. Investigations based on density functional theory reveal that the above reactions occur through an interesting sequence. An initial CO or NO adsorbed on the Fe_2O_3 weakens one of the O-Fe bonds to create a loosely attached O site. A subsequent CO gets oxidized by this O and transforms the cluster to a reduced Fe_2O_2 that now reduces NO via multiple oxidation and reduction steps that return the cluster to the oxidized Fe_2O_3 state. It is shown that the small size allows geometrical rearrangements that eliminate reaction barriers, allowing energetics and not barriers to be the primary motor for catalysis. Detailed reaction paths and the corresponding energetics are presented to illustrate the viability of the proposed mechanisms.

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CO and NO are undesirable chemical products in automobile exhausts, cigarette smoke, and other industrial processes and their removal is one of the important industrial and environmental problems involving acid rain, stratospheric ozone, and greenhouse gases [1]. In particular, there is considerable interest in finding systems that could promote NO reduction by CO to achieve the dual task. Since the CO molecule has a strong binding energy of 11.23 eV (experimental), the CO elimination [2] usually proceeds via oxidation to produce CO_2 . On the other hand, NO is bound only by 6.51 eV and N_2 is a strongly bound molecule with an experimental binding energy of 9.76 eV. NO removal is therefore usually accomplished via reduction [3] to form N_2 . The ideal situation would then be if the CO oxidation could be carried out by NO reduction, as this would achieve the dual task. It has been found that this can indeed be possible [3,4], for example, by Pd particles or monolayers supported on MgO. The key steps in the reaction are the breaking of the NO molecule and a subsequent oxidation of the CO. The dissociated N atoms then recombine to form N_2 . However, it is found that on these catalytic surfaces the NO dissociation is difficult at low temperatures while the CO adsorption is difficult at high temperatures. The reaction rate is, therefore, limited by these constraints. What would be ideal is to find a system where CO adsorption could facilitate NO dissociation so that the combined reduction is collectively stimulated. It has been proposed that transition metal oxides may present such systems. Indeed, Randall *et al.* [5] have recently experimented with the CO-NO reaction over a silica supported iron oxide catalyst. Their studies show that while the NO reduction occurs readily over reduced oxide Fe_3O_4 , the CO oxidation occurs over the oxidized catalyst (Fe_2O_3). The fact that different compositions stimulate

different reactions suggests that it would be ideal to have a catalyst which is stable over a wider range of compositions.

The purpose of this Letter is to show that small clusters of Fe_2O_3 may be a potential candidate for CO-NO reactions. Wang *et al.* [6] have recently generated Fe_nO_m clusters containing up to four Fe and six oxygen atoms in molecular beams and have carried out negative ion photodetachment spectroscopy that can help identify their geometrical forms in conjunction with theory. Their results indicate that it is possible to form clusters over a wider range of compositions than in solids. Further the atomic rearrangements are far easier in smaller sizes. Both these suggest that clusters may be a potential candidate for the proposed reactions [7]. Our detailed theoretical studies carried over a Fe_2O_3 cluster indeed confirm this optimism. As we showed in a recent paper [8], this cluster can oxidize CO via an interesting mechanism. The original cluster has three O atoms bound to both Fe atoms. An initial CO attaches to a Fe site and breaks one of the Fe-O bonds. The less bound O easily oxidizes another oncoming CO leading to a reduced iron oxide cluster. As we show in this Letter, this resultant cluster is ideal for NO reduction. Here an initial NO adsorbed on the low coordinated Fe site has enough heat of adsorption to stretch NO bonds. What is interesting is that a stretch of the NO bond to just 1.30 Å from its initial value of 1.17 Å allows an approaching CO to form CO_2 in a barrierless reaction leaving behind an N atom bound to a Fe site. An approaching NO then forms N_2O and the heat of adsorption is sufficient to allow N_2 to leave the cluster returning the system to the oxidized form and ready to reoxidize CO. What is most remarkable is that, during the catalytic process, the underlying cluster undergoes compositional changes that optimize its ability to oxidize CO or to

reduce NO. Further, the finite size facilitates structural rearrangements that help reduce the reaction barriers.

The theoretical investigations were carried out using the DMOL set of codes (density functional electronic structure program from Accelrys, Inc.) [9] designed to carry out first principles density functional calculations [10]. The basic idea is to express the molecular orbitals as a linear combination of atomic orbitals centered at the ionic cores. In the DMOL implementation, the atomic orbitals are taken as the orbitals of the free atoms/ions on a radial mesh of points. The Hamiltonian matrix elements entering the solution of the Kohn-Sham equations are calculated via numerical integrations over a mesh. It is important to realize that the atomic orbitals are not fitted to auxiliary functions such as Gaussians, and therefore the shapes of the atomic orbitals in the core region are accurately described. In addition, our basis sets included polarization functions to accurately describe changes in atomic orbitals in the valence region during the formation of clusters. In this work, we used the double numerical basis sets with $4p$ polarization functions for Fe and $3d$ polarization functions for C, N, and O. The exchange correlation corrections were included via a gradient corrected density functional. Here, we have used the functional proposed recently by Perdew *et al.* [11]. For other details, the reader is referred to earlier papers.

We begin with pure Fe_nO_m clusters. In Fig. 1 we show the ground state electronic properties of Fe_2 , Fe-O, Fe_2O_2 , and Fe_2O_3 clusters. Our calculated ground state of Fe_2 is a spin septet with a bond length of 2.00 Å. These are in good agreement with the previously calculated and experimental values of 7 and 2.02 Å, respectively [12]. For Fe-O, the ground state multiplicity and bond length are 5 and 1.62 Å. These values are again close to the experimental values of 5 and 1.62 Å, respectively [13]. The ground state of Fe_2O_2 is a planar structure, as shown. There are no Fe-Fe bonds. For Fe_2O_3 , the ground state with an O_3 complex is a distorted triangular bipyramid with two Fe atoms at the apex sites while the O atoms decorate the triangular base. Another structure (not shown in Fig. 1) corresponding to an O atom bound to an Fe_2O_2 unit is also very stable. Our calculated binding energy (BE) for Fe-O is 6.60 eV compared to 3.65–5.29 eV obtained in other density functional calculations [13] and the experimental value of 4.17 eV. For the DMOL approach used here, while an excellent approach for calculating energy differences, the absolute binding energies are not as good. This is because the BE calculations require atomic reference energies that are not as accurate. To further demonstrate that the differences in energies are accurate, we calculated the ionization potentials of Fe-O and Fe_2O_2 . Our calculated values of 9.12 eV for Fe-O and 8.47 eV for Fe_2O_2 are in good agreement with the corresponding experimental [14] estimates of 8.9 ± 0.16 and

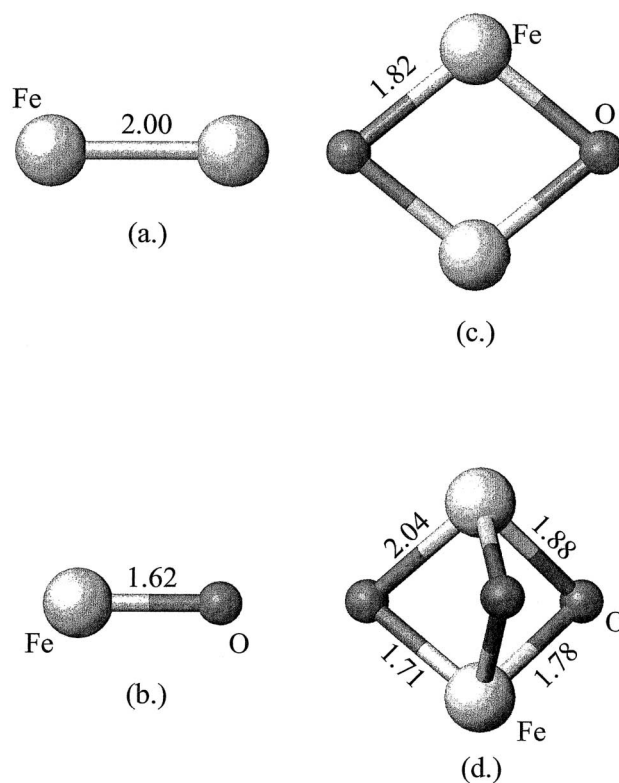


FIG. 1. The ground state geometries of bare Fe_nO_m ($n = 1, 2$ and $m = 1-3$) clusters. The bond lengths are in Å.

8.40 eV for Fe-O and Fe_2O_2 , respectively. The calculated bond length and multiplicity are also consistent with earlier studies [6].

In order to consider the CO-NO reaction, we plot the reaction energetics in Fig. 3 and we show the geometries of the corresponding intermediate steps in Fig. 2. Consider the case where an initial CO approaches the Fe_2O_3 cluster; it can bind to the Fe site or combine with an O to form CO_2 . A study of the energetics shows that the attachment to Fe is more favorable than going to O by 0.38 eV. In our calculations, the CO binding to a Fe site has the binding energy of 3.17 eV that lowers the total energy as shown in Fig. 3. Note that the original cluster had three O atoms, each bound to the two Fe sites. What is interesting is that, as a CO is attached to a Fe site, one of the O's originally bonded to both the Fe sites breaks its bond with the Fe site to which the CO is attached, resulting in the final structure shown in Fig. 2(a). Another CO approaching the ensuing cluster now favorably binds to the less coordinated O atom, forming the CO_2 molecule as shown in Fig. 2(b). As shown in a previous study [8], this reaction proceeds in a barrierless manner. In addition, the heat of formation is sufficient to evaporate the CO_2 molecule that leaves the cluster. The corresponding energetics are shown in Fig. 3. The low coordinated Fe site is the active site to carry out further catalytic reactions. It

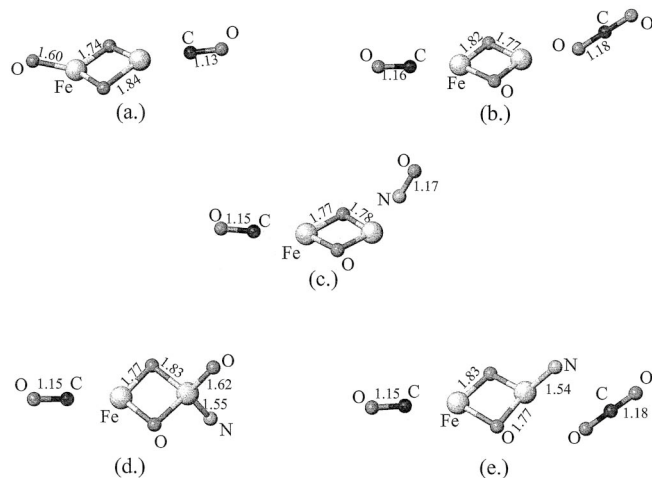


FIG. 2. The ground state geometries of various CO and NO adsorbed Fe_2O_3 clusters marking the oxidation of CO and reduction of NO: (a) $\text{CO-Fe}_2\text{O}_3$; (b) $\text{CO-Fe}_2\text{O}_2\text{-CO}_2$; (c) $\text{CO-Fe}_2\text{O}_2\text{-NO}$; (d) $\text{CO-Fe}_2\text{O}_2\text{-N---O}$; (e) $\text{CO-Fe}_2\text{O}_2\text{-N-CO}_2$.

can be occupied by a CO or an NO molecule. As shown in a previous study [8], a subsequent CO attached to this site can undergo oxidation via an approaching O_2 . Here, we focus on the case of NO. For a single NO approaching the cluster, the most favorable (energetically lower) path corresponds to an NO approach to the less coordinated Fe site. The ground state corresponds to an NO bound to the Fe site as shown in Fig. 2(c) with a gain in energy of 2.40 eV as shown in Fig. 3.

The key issue is to examine the conditions that would favor the reduction of this NO by an approaching CO. To this end, let us first examine the energetics of the reaction

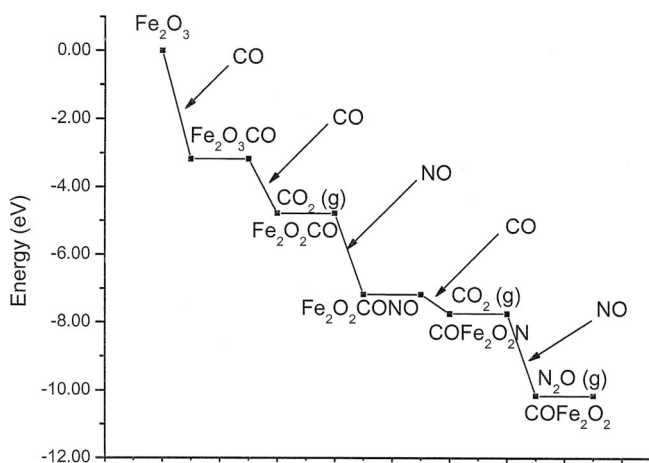
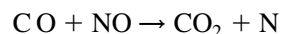


FIG. 3. The energies of the various reaction processes shown in Fig. 2. All energies are in eV. $\text{CO}_2(\text{g})$ and $\text{N}_2(\text{g})$ respectively correspond to CO_2 and N_2 leaving the cluster after the formation.



in free CO and NO. In free molecules the sum of the calculated binding energies of CO and NO is 19.50 eV, while the binding energy of a CO_2 molecule is 18.64 eV. From energetics alone, such a reaction would require 0.86 eV to occur. On the other hand, if the NO molecule is bound to a cluster and the binding energy of N alone is more than 0.86 eV, the reaction should be allowed on energetic grounds. The energetic balancing is, however, insufficient, as the chemical reactions involve barriers. In fact, the whole purpose of the catalyst is to lower this barrier to facilitate the reaction. In the present case, the reduced iron oxide cluster precisely does that.

In order to understand the role played by an iron oxide cluster, it is important to realize that the heat of adsorption of the NO will drive the system to structural arrangements of higher energy different from the ground state. For example, the configurations where the NO bond would be stretched and possibly broken may be possible. The question one wants to ask is how the reaction barriers are affected by such a stretch. To examine this, we started with the reduced cluster with one NO and investigated the reaction path for the oxidation of an approaching CO for various stretched NO distances. For each calculation, the initial NO distance was stretched and a CO was allowed to approach the stretched NO. The prime motivation is to determine an NO configuration that would allow a barrierless CO oxidation. Interestingly, we found that if the NO were stretched to just 1.30 Å from its equilibrium bond length of 1.17 Å, the reaction proceeded without any barrier. What is even more interesting is that the energy required to stretch the adsorbed NO to 1.30 Å is only 0.78 eV, far less than the heat of adsorption. This shows the microscopic nature of the catalytic phenomenon. The heat of formation allows structural deformations that in turn allow reaction pathways otherwise inaccessible under ordinary conditions. To further ascertain that our findings are not affected by the choice of basis set or the numerical procedure, we carried out a supplementary calculation using the NRLMOL (Naval Research Laboratory Molecular Orbital Library) set of codes [15–17] that use Gaussian basis sets and are known to provide accurate binding energies. A CO molecule was placed 3.35 Å from the Fe site in a $\text{CO-Fe}_2\text{O}_2\text{-NO}$ where the O of NO was 1.46 Å from the C of CO. The CO molecule combined with O of NO to form a CO_2 that eventually left the cluster.

We also examined if a completely dissociated state of NO was accessible. To this end we calculated the energy of the $\text{CO-Fe}_2\text{O}_2\text{-NO}$ system shown in Fig. 2(c) as the NO bond is stretched. The NO dissociated structure is shown in Fig. 2(d). We found that the breaking of NO has a barrier of 3.14 eV that is less than the energy gained due to the combined heat of formation of the NO and the

previous CO (see Fig. 3). Consequently, there is enough energy to overcome the barrier. The key is that both stretching or breaking the NO bond set the stage for a CO-NO reaction. The approaching CO combines with O to form CO₂ that again leaves the cluster that has only one N attached to the Fe site. The corresponding geometry and the energetics are shown in Figs. 2(e) and 3.

The final step in the reaction then is the reduction of an approaching NO molecule. Our studies indicate that the NO molecule approaches the cluster with the N end towards the Fe site bound to the N atom. As the N end of the approaching NO molecule comes within 1.60 Å of the N atom of the cluster, the highly exothermic reaction of the N atoms combining to form N₂O takes place. The enormous heat of the reaction allows the newly formed N₂O to break into N₂ and O. N₂ can then be released from the cluster leaving behind the O atom and returning the cluster to the configuration 2(a). The reaction then proceeds as before.

In the above discussion, we started with a CO approaching the Fe₂O₃ cluster. One could ask what would happen if an NO approaches the initial cluster. A single NO was brought towards the Fe or O site and the energy optimized. The lowest energy configuration corresponds to the NO bound to a Fe site. Interestingly, as the NO binds to the Fe site, one of the O atoms breaks the bond to this Fe site and the ground state of the NO-Fe₂O₃ cluster is like that of the CO-Fe₂O₃ in that an O atom is bound only to one Fe as shown in Fig. 2(a). The subsequent reactions then proceed in pretty much the same sequence. This shows that the reaction can be initiated by either a CO or an NO molecule.

The above results bring out an interesting feature. The CO oxidation occurs in configuration where the iron oxide has a Fe₂O₃ configuration arising as in initial CO-Fe₂O₃ or CO-Fe₂O₂-NO where the NO bond is stretched. On the other hand, NO reduction proceeds in reduced configurations like CO-Fe₂O₂-N. One could ask if the NO reduction can also occur in configurations “Fe₂O₃” as in CO-Fe₂O₃ or CO-Fe₂O₂-NO. In the case of CO-Fe₂O₃, the NO merely attaches to the Fe site not bound to CO. An additional NO coming towards the bound NO site to undergo reduction to form N₂ is not feasible, as it would leave to create an Fe site bound to four O atoms, which is energetically unfavorable. We believe that this feature is consistent with observations on iron oxide nanoparticles which indicate that, while Fe₂O₃ nanoparticles can oxidize CO, reduced oxides such as Fe₃O₄ are needed to reduce NO.

To summarize, we have shown that small Fe₂O₃ clusters could form ideal catalysts for CO oxidation and NO reduction. Note that the bare cluster is unable to carry out the reaction, and an initial adsorption of CO or NO is

needed to start the catalytic process. In this respect, one could call the reaction self-stimulated. What is truly unique in the process is that the same cluster undergoes changes in the oxidation state that favor CO oxidation or NO reduction. This shows that the reacting species themselves act as promoters of the reaction. In addition, the ease of rearranging the geometrical configuration helps lower the barriers, e.g., for NO dissociation. We add that, while the present studies are carried out on small clusters, many of the arguments are fairly generic and could be applicable to larger systems. Also, for practical applications, the clusters need to be supported and one has to worry about the effect of support. We hope that the present work generates interest in carrying out experimental studies of catalysis on size-selected clusters.

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