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Oxygen on Iron Oxide: Kinetic Evidence of an Atomic Species

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Oxygen adsorbed on α-Fe_2O_3 in three different forms over the temperature range from 450°C to room temperature. The form that adsorbed and desorbed between 200 and 300°C desorbed with a second-order kinetics which suggested its atomic nature. The activation energy of desorption was found to be 163 ± 8 kJ/mole, and the initial coverage at 240°C was 1.4×10^{16} molecules/m^2. It was postulated that the adsorption and desorption of this species involved pairs of surface iron ions containing coordinative unsaturation, while surface mobility of the species was provided by single surface iron ions.

INTRODUCTION

In the oxidation of many hydrocarbons, the desired products and the total combustion products often differ primarily in the extent of incorporation of oxygen into the molecule. For this reason, the yield of the selective oxidation product depends critically on the nature of the reactive surface oxygen species. Thus studies in this area often aim at the question of whether the active oxygen is a chemisorbed species or a lattice oxygen, whether it is atomic or molecular oxygen, and what is the strength of interaction of the oxygen with the catalyst.

Whether chemisorbed or lattice oxygen is the active species has been investigated most intensively in the oxidation of propene on bismuth molybdate (*1–3*). The most current belief is that lattice oxygen participates heavily at higher temperatures in the production of acrolein, while the contribution due to chemisorbed oxygen increases at lower temperatures (*3*). Perhaps the surface–oxygen bond strength differs only slightly for the chemisorbed and the lattice oxygen such that the difference in thermal energy at different temperatures is enough to promote one or both species into the precursor state for reaction. Indeed, the surface–oxygen bond strength has long been postulated as an important parameter that determines the selectivity and the activity of a catalyst. In general, it is believed that the selectivity for partial oxidation follows a volcano-shaped curve with respect to the surface–oxygen bond strength. When the bond strength is very strong, the surface oxygen is too inert for oxidation reaction. When it is too weak, the surface oxygen is too reactive, so that combustion dominates. Thus the yield of the intermediate product is the highest at intermediate bond strength. This concept has been shown to be valid in the oxidative dehydrogenation of butene to butadiene (*4*). The correlation between the activity in hydrogen and methane oxidation and the bond strength can also be viewed as an indirect support of this concept (*5, 6*). While the concept is generally accepted, there is disagreement as to what is the best measure of the surface–oxygen bond strength. Often this surface parameter is being approximated by bulk parameters such as the heat of formation or the heat of reduction of the oxide (*7*).

The role of atomic and molecular oxygen is another interesting question. Unfortunately this has been thoroughly studied only on a limited number of systems such as the oxidation of ethylene to ethylene oxide.

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In this reaction, it has been suggested that atomic oxygen on the silver catalyst causes combustion reaction, while molecular oxygen is responsible for partial oxidation, although definitive data have yet to be obtained (*8*, *9*).

Iron oxide (α-Fe_2O_3) has been shown to be a selective catalyst for the oxidative dehydrogenation of butene to butadiene (*4*, *10*, *11*). Recent studies using temperature-programmed desorption technique showed that oxygen chemisorbs on iron oxide in at least three different states of different desorption kinetics (*12*, *13*). In view of the possible importance of these species in the oxidation reactions, it is of interest to elucidate which of these species are atomic or molecular, and their binding strength on the surface. The latter can be estimated from the activation energy of desorption which, unfortunately, can only be obtained easily from temperature-programmed desorption data for first-order desorption. We report here the characterization of what we believe to be an atomic chemisorbed oxygen species on iron oxide with emphasis on its strength of interaction with the surface as deduced from the desorption kinetics. In a forthcoming publication, the reaction of this species with butene will be described.

EXPERIMENTAL

Iron oxide was prepared as before (*11*) by precipitation with ammonium hydroxide from a solution of iron nitrate. After thorough washing, the precipitate was dried at 80°C, ground to a fine powder, and then heated at 525°C twice for a total of 7 h. The nitrogen BET area was 17.1 m^2/g.

In the preliminary runs, 0.2 to 1 g of catalyst was used. Most of the data reported here were obtained with about 0.3 g of catalyst which was considered optimal after considering the amount of oxygen adsorbed, the amount of oxygen contamination due to leakage from the ambient and as impurity in the carrier gas, the degree of readsorption of desorbed oxygen, and the effectiveness of purging the reactor clean after oxygen adsorption. Detailed knowledge of these effects was important because of the very small amount of oxygen being measured. Readsorption was concluded to be unimportant under our operating conditions in which kinetic data were obtained from data obtained with different carrier flow rates and with different amounts of catalysts.

Experiments were run in a quartz flow reactor. Typically, the catalyst which was sandwiched between quartz wool plugs was pretreated by heating in flowing He (40 ml min^{-1}) at 450°C for 0.5 h. Oxygen was then adsorbed onto the catalyst by passing a stream of oxygen (40 ml min^{-1}) over the catalyst at 300°C for 0.5 h. Sometimes other adsorption temperatures were used. Afterward the temperature was lowered to 240°C and the reactor was purged with helium for 2 h. Other purging temperatures and times had been used and they will be appropriately mentioned. After purging, in some experiments, the amount of oxygen that remained adsorbed can be determined by thermal desorption that was achieved by raising the temperature at 10° or 15°C/min to 430°C. The catalyst was held at 430°C sufficiently long to ensure complete desorption. The oxygen released was collected downstream by a silica gel trap at −196°C. Later the trap was warmed to room temperature and the quantity of oxygen collected was analyzed gas chromatographically.

In some other experiments, isothermal desorption was performed after purging. In these cases, the catalyst temperature was changed to the desorption temperature after purging, and the oxygen desorbed from the catalyst was collected by the silica gel trap downstream at −196°C for analysis afterward as described above. At the end of the isothermal desorption, the amount of oxygen still left adsorbed was determined by thermal desorption to 430°C in the same manner as that described above.

The reactor with quartz wool but without catalyst was shown not to adsorb oxygen when exposed to oxygen below 450°C. The helium carrier used was purified by a silica gel trap at −196°C, and the oxygen was purified by a silica gel trap at −78°C.

RESULTS

With the small amount of catalyst used, the amount of chemisorbed oxygen was very small. It became important to determine the condition at which the oxygen collected at the reactor outlet represented mostly desorbed oxygen and not residual gas phase oxygen left after adsorption or oxygen from leak or in the helium stream. To determine the effectiveness of purging the reactor of oxygen after adsorption, we filled the reactor with argon and purged it with helium. The argon exit from the reactor was collected and measured. Figure 1 shows the amount of argon collected over 15-min intervals after the commencement of purging. Two sets of data that have been reproduced are shown, one for an empty reactor and one for a reactor containing about 0.3 g of iron oxide. The empty reactor was purged clean slightly more rapidly. If oxygen was used instead of argon in the empty reactor, the behavior was qualitatively the same except that the entire curve was shifted upward by an amount of about 0.5×10^{16} molecules/15 min, which is the rate of oxygen collected at the reactor outlet due to leakage from the atmosphere and the impurity in the helium gas. For oxygen with a reactor with catalyst, the decay of the curve was slower due to desorption from the sample.

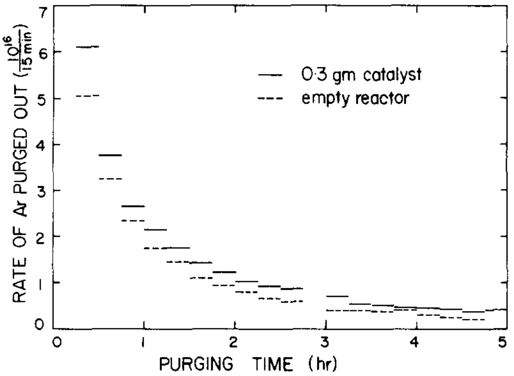

FIG. 1. Rate of Ar collected at the reactor outlet over intervals of 15 min as Ar was being purged out by He at room temperature. Solid line is for one with catalyst in place, broken line is for one without catalyst.

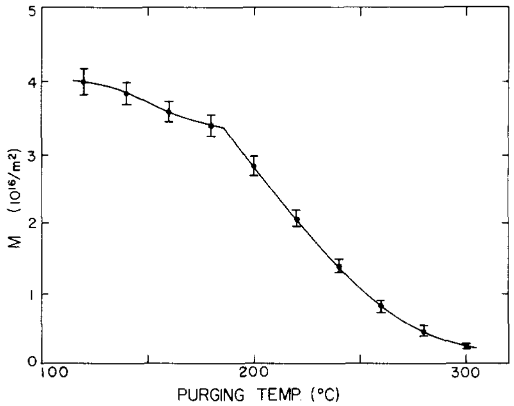

FIG. 2. Amount (M) of adsorbed oxygen left on the surface after purging for 4.5 h at the purging temperature. Adsorption was achieved by exposure to oxygen at 300°C and then cooled to the purging temperature.

From this figure, it can be seen that the oxygen content in the gas phase in the reactor fell to within twice the value from leak and impurities after purging for 2 h, and it was less than 15% of the value of the desired signal of desorbed oxygen. In the kinetic data described later, the contribution to the observed signal from this physical effect had been subtracted.

If a catalyst was exposed to oxygen at 300°C for 20 min and then cooled to a lower temperature for purging, the amount of chemisorbed oxygen at the end of a long purging, as determined by thermal desorption afterward, varied with the purging temperature in the manner shown in Fig. 2. The amount left chemisorbed decreased with increasing purging temperature as expected. Interestingly the curve appeared to have a break point at about 190°C that probably indicated the presence of two different chemisorbed species. Similar indication was provided by another series of experiments in our preliminary runs, the results of

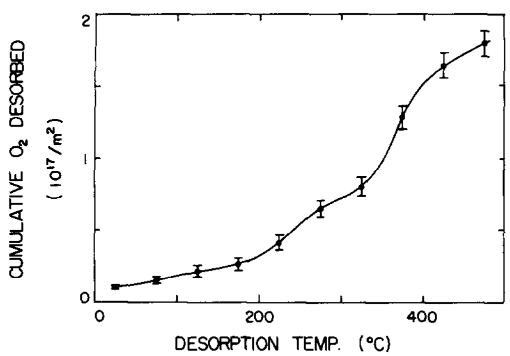

FIG. 3. Cumulative amount of oxygen desorbed as a function of increasing desorption temperature. Adsorption was by exposure to oxygen at 450°C and then cooled to room temperature in oxygen.

which are shown in Fig. 3. In these experiments, after the pretreatment, the catalyst was cooled in oxygen from 500°C to room temperature at 10°C/min. After purging the helium at room temperature for 20 min, the temperature was increased in 50°C intervals to achieve thermal desorption. The temperature was held at each value for 1 to 3 h until little further desorption of oxygen was detected before it was raised to the next value. The amount of oxygen desorbed at each interval was determined, and the cumulative amount desorbed is shown in Fig. 3.

Since the selective oxidation reaction is often conducted between 200 and 300°C, the species that adsorbs and desorbs in this temperature range is of particular interest. Results of Figs. 2 and 3 suggested that the oxygen species that adsorbed and desorbed in this temperature range was probably one species, which was consistent with the ear-

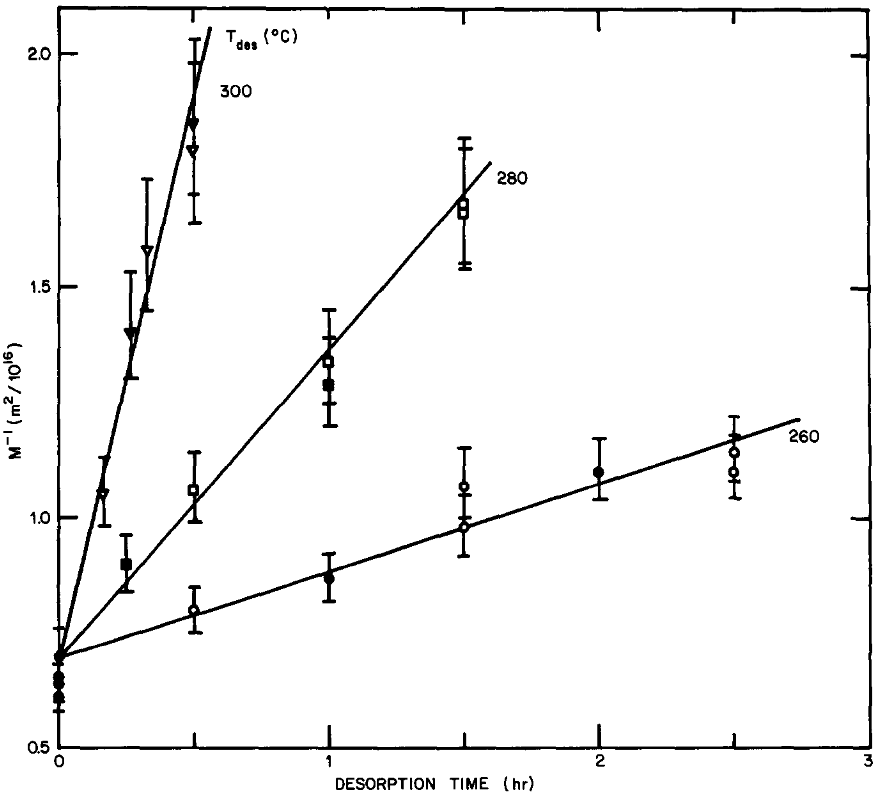

FIG. 4. Reciprocal of the amount (M) of adsorbed oxygen left on the surface after the indicated desorption time. Adsorption was by exposure to oxygen at 300° and then 240°C. The catalyst was purged by He at 240°C for 2 h before desorption began. The filled and the empty data points indicate different samples of catalyst.

lier results (*12, 13*). The kinetics of its desorption was then measured.

Adsorption of this oxygen species was achieved by exposing the catalyst to flowing oxygen at 300°C for 0.5 h. The catalyst was then cooled to 240°C in O_2 and purged at this temperature by He for 2 h. At the end of purging, the temperature was adjusted to the desired value for isothermal desorption. After that the amount of oxygen left on the surface was determined by thermal desorption to 430°C. This amount was shown in Fig. 4 for different isothermal desorption times and temperatures. Similar experiments had been performed using a purging temperature of 200 or 220°C instead of 240°C, and the corresponding data are shown in Fig. 5.

The data in Fig. 4 were plotted assuming that the isothermal desorption followed a second-order kinetics. The linear relationship among the data points suggests that the assumption is probably valid. From the slopes of the plot, a desorption rate constant for each temperature can be calculated. An Arrhenius plot of these rate constants yielded an activation energy of 163 ± 8 kJ/mole (Fig. 6).

DISCUSSION

We shall first discuss the general aspect of the results here and then in detail the species whose desorption kinetics was characterized.

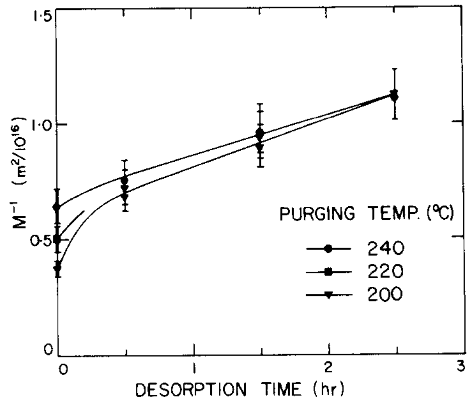

FIG. 5. Reciprocal of the amount (M) of adsorbed oxygen left on the surface after the indicated desorption time. Conditions were the same as those for Fig. 4 except that different purging temperatures were used. The desorption temperature was 240°C.

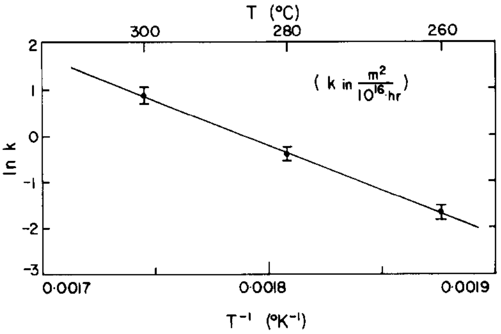

FIG. 6. Arrhenius plot of the data shown in Fig. 4.

The oxygen species reported here are chemisorbed species and not from the vaporization of lattice oxygen. This is because there was practically no desorption from the sample that had undergone an identical treatment except without exposure to flowing oxygen. Thus the desorbed oxygen that we measured must be from those adsorbed when the sample was exposed to oxygen. Since our samples had been pretreated in helium at 450°C, the observation was expected.

Data in Figs. 2 and 3 show that there are at least three adsorbed oxygen species on iron oxide of different desorption kinetics. This has also been observed by Iwamoto *et al.* by temperature-programmed desorption experiments (*12*) which had been largely reproduced by us (data not shown), and by Halpern and Germain (*13*). Iwamoto *et al.* also reported that the species desorbing at the lowest temperature showed varying desorption characteristics depending on the adsorption condition. Such a phenomenon was also observed here.

The fact that the data in Fig. 4 for a purging temperature of 240°C followed well a simple second-order kinetics suggested that these data were from a single oxygen species. In contrast, for lower purging temperatures (Fig. 5), the desorbed species contained a second species in the beginning. After this second species was depleted, the desorption kinetics indicated a simple second order again. This was consistent with data of Fig. 2.

The species that desorbs with a second-order kinetics is likely adsorbed atomic oxygen. When two atomic oxygen recombine to form a molecule on desorption, it is natural that the desorption kinetics is second order in the concentration of adsorbed oxygen. This is true provided that the surface is homogeneous. The fact that the simple kinetics appeared to hold over a threefold change in surface concentration suggested that perhaps the surface is indeed homogeneous for this process. The work reported by Winter on oxygen exchange with oxides supported this assignment of atomic species (*14*). He observed that the homomolecular exchange reaction $^{16}O_2 + {}^{18}O_2 \rightleftharpoons 2{}^{16}O^{18}O$ took place at about 300°C on a degassed α-Fe_2O_3 that had been pretreated in a similar manner. Such homomolecular exchange can be easily understood if the gas phase oxygen adsorbs dissociatively.

Iwamoto *et al.* on the other hand assigned a similar species to molecular oxygen (*12*). Their evidence was from the fact that the temperature-programmed desorption peak of this species did not appear to shift with changing peak size. However, they mentioned that no experiments were performed to confirm it. It is possible that ours and theirs are two different species. It is also possible that in their temperature-programmed desorption experiments, the relatively large amount of catalyst (~1 g) resulted in significant readsorption. The resulting broadening of the peaks masked any shift in the peak position. We tend to favor the latter explanation. The molecularity of the desorbed species was not investigated by Halpern and Germain (*13*).

This second-order kinetics also suggested that the atomic oxygen is mobile on the surface. The dissociative adsorption of molecular oxygen to form this species should not take place on an isolated surface iron ion with one coordinative unsaturation. Such a center would adsorb oxygen molecularly as in many transition metal complexes and oxygen carrying proteins (*15*). Rather the adsorption probably takes place on centers involving two adjacent surface iron ions. In corundum α-Fe_2O_3, the bulk ions are situated in a distorted octahedral arrangement of oxygen neighbors. Some of these octahera are corner-sharing, some are edge-sharing, and some are face-sharing. We believe that the adsorption occurs on a pair of surface iron ions that are either in edge-shared or face-shared octahedra, as schematically shown in Fig. 7. The necessary coordinative unsaturation is obtained as shown by removing the oxygen ions at the appropriate corner of the octahedra in forming the surface. During adsorption, the oxygen molecule would approach the site at the coordinatively unsaturated point. It is then dissociated to yield one oxygen atom for each iron ion. It is interesting to note that the two surface sites shown can be partially interconverted through buckling of the metal–oxygen–metal plane. Perhaps in the real surface, the surface layer is indeed buckled to allow stronger interaction between the adjacent metal ions to lower the surface energy, making the site look like that shown for face-shared octahedra. Adsorption of oxygen would satisfy the coordinative unsaturation. The surface layer then flattens out and the site may look more like the one for edge-shared octahedra. The two sites are not truly interconvertible because of different atomic arrangements surrounding them.

After adsorption, the atomic oxygen is mobile on the surface by jumping from one

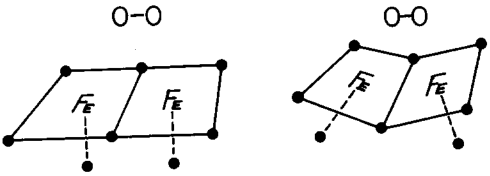

FIG. 7. Model of the adsorption and desorption site for dissociative adsorption. Solid circles represent lattice oxygen. On the left is shown a pair of edge-shared octahedra, on the right a pair of face-shared octahedra.

coordinatively unsaturated surface iron ion to another. These surface iron ions do not have to occur in pairs for mobility. However, occasionally two such ions meet to form a pair, desorption of oxygen molecule can occur if both ions carry an oxygen atom. The reverse process of adsorption occurs if both ions are not occupied and there is gas phase oxygen present. Once the adsorbed oxygen dissociates into the atomic form, it loses its identity by exchanging with the lattice oxygen. This exchange process is known to occur readily under these experimental conditions (*14*).

In this model, the observed kinetics of second order in adsorbed oxygen can also be viewed as second order in surface ions carrying an atomic oxygen. The maximum coverage of adsorbed oxygen is then the maximum concentration of coordinatively unsaturated surface ions, if charge transfer is not the limiting factor. From the rate constant and the amount of adsorbed atomic species left at the end of purging, the initial coverage of this species after adsorption can be calculated. At 240°C, this initial coverage was found to be 1.4×10^{16} molecules/m^2. This compares well with the values of 2.3 to 4.5×10^{16} molecules/m^2 reported by Iwamoto *et al.* (*12*). This represents less than 1% of a monolayer, suggesting that the concentration of surface unsaturated ions is low. Such ions may indeed be localized at the imperfect regions of the crystal surface such as grain boundaries. Alternatively, the low initial coverage may be due to the charge transfer accompanying adsorption. Such charge transfer would build up a space-charge barrier which tends to hinder further adsorption. The amount of charge transfer required before adsorption stops is small for insulating compounds such as the iron oxide used here.

Theoretical calculations had been performed on clusters representing the surfaces of TiO_2, $SrTiO_3$, and NiO to understand chemisorption on these surfaces, and on oxo-clusters of chromium and tungsten. On the TiO_5 and the oxo chromium and tungsten clusters, interaction of oxygen with the transition metal center was believed to be through the *d* orbitals of the metal center in a manner very similar to the metal–ligand interaction of low valent noble metal inorganic complexes (*16, 17*). This probably also applies to oxygen adsorption on iron oxide. Another feature suggested by TiO_5 and NiO_5 cluster calculations is that Ti and Ni in their most stable oxidation states of +4 and +2, respectively, are probably inactive in chemisorption. The active species are those of lower valence state (+3 and +1, respectively) that are formed because of surface defect, such as anion or cation vacancies (*16, 18*). Such a view is in general agreement with experimental observations on clean surfaces studied in ultrahigh vacuum systems (*19–21*). We believe that this is also important here. Thus the oxidation state of the iron centers is likely to be less than +3. Adsorption of oxygen would be accompanied by some charge transfer to the oxygen, bringing the oxidation state closer to 3.

The activation energy for desorption was found to be 163 kJ/mole. That reported by Iwamoto *et al.* was about 100 kJ/mole (*12*). We do not have an explanation for the difference except the discussion presented earlier on the desorption order. On the other hand, the value reported by Halpern and Germain was about 164 kJ/mole (*13*), in close agreement with ours. This activation energy is larger than the heat of adsorption by the activation energy of adsorption. This latter quantity is nonzero as we found that the amount of atomic oxygen adsorbed decreased with decrease in adsorption temperature over the range from 200 to 300°C. That adsorption of the atomic species is activated has also been reported earlier (*12*).

It is interesting to compare this activation energy with other related quantities involving oxygen and iron oxide. In particular, Boreskov *et al.* measured the heat of vaporization of oxygen from iron oxide (*5*). Their sample pretreatment was similar to ours except that the oxide was cooled in oxygen from 500 to 50°C at which temperature the reactor was evacuated. Judging from our data, their sample surface should contain all three types of oxygen observed here. Interestingly, the equilibrium vapor pressure of oxygen apparently followed the Clausius–Clapeyron equation for a single species, and the heat of vaporization was found to be 138–164 kJ/mole over a 3% monolayer variation of surface coverage of oxygen. The absence of apparent inhomogeneity in their result may be due to the fact that under their experimental conditions (primarily the temperature range), only one majority species was being investigated. Unfortunately, insufficient detail was provided in their report for more definitive conclusions. Judging from their experimental conditions, if indeed they were observing only one species, it is likely that they were studying the atomic species reported here. If so, their heat of vaporization is consistent with our activation energy of desorption allowing for the activation required for adsorption.

In view of the characteristics of this atomic species, one could postulate its role in selective oxidation reactions. Since its heat of adsorption and activation energy for desorption are rather large, it could only participate directly in reactions that have large heats of reaction, that is, in reactions where bonds are formed with large release of energy. Combustion reactions would satisfy this. Selective oxidations in which oxygen is incorporated into the product would probably not. The species could also participate indirectly by blocking the active sites which are often believed to be the exposed iron ions (*22–24*). Results of our study to investigate this will be reported in the future.

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