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Reactive intermediates formed upon electron transfer from the surface of oxide catalysts to adsorbed molecules

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Abstract

The basic steps of catalytic oxidation processes at the surface of metal oxides consist in redox interactions involving the solid and one or more reactants (in particular molecular oxygen). The general redox properties of a metal oxide can be investigated by means of the electron paramagnetic resonance (EPR) technique which is capable of detecting the paramagnetic centers often formed upon one electron redox processes. The principles of the EPR technique are briefly described in the first part of this paper. In the second part routine methods to measure the electron donor and the electron acceptor ability of a surface (using particular probe molecules) are described. Finally the paper deals with the interactions of molecular oxygen with the surfaces of oxides leading to electron transfer towards the adsorbed molecule. Various examples of electron transfer are discussed in relation to the nature and activation conditions of the solid. In conclusion the particular case of surface intermolecular electron transfer (SIET) is briefly illustrated.

Keywords: Oxides; EPR; Electron transfer

1. Introduction

The main chemical interactions between the surface of an oxide catalyst and a molecule are well known from general chemistry. They can be schematically resumed as follows:

1. *Acid–base interactions*. These can be either of Broensted or Lewis type involving proton exchange or electron pair donation, respectively. When the solid acts as a proton donor or as an electron pair acceptor the field of acid catalysis is considered. In the opposite case one deal with basic catalysis.
2. *Coordination chemistry interactions*. These interactions usually occur when transition metal ions (TMI) are present in the catalyst or are anchored at the surface of a support and can go from the simple coordination of a ligand in the coordination sphere of the TMI to more complex processes involving activation of the ligand molecule by interaction with d orbitals of the metal ion itself. Several catalytic processes such as oligomerizations, polymerizations and some kinds of oxidation occur by means of processes involving, at least in one step, coordination chemistry interactions.
3. *Redox interactions involving the exchange of electrons between the solid and the adsorbed molecules*. As it will be shown in the following such interactions are particularly important in oxidation

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catalysis or in particular processes like NO_x selective reduction.

The previous list is certainly not exhaustive (weak van der Waals interactions, for instance, play very often a role in some step of a catalytic processes) but it can considered a first preliminary scheme to rationalize the complex field of surface chemistry and catalytic chemistry of oxides.

Redox interactions at the surface of oxides are the object of the present contribution which will illustrate some selected example essentially involving the chemistry of oxygen and are therefore related, in general terms, to the field of oxidation catalysis.

Since the electron transfer between an oxide surface and an adsorbate is, in most cases, a one-electron process it is easily understandable that radical centers are quite usually formed as a consequence of the electron exchange. It is therefore not surprising that the electron paramagnetic resonance technique (EPR) has become a leading technique to study the surface-adsorbate redox chemistry. This technique is briefly illustrated in the next section.

Then, after a section discussing in general terms the problem of the interaction of oxygen with the surfaces of oxides, a series of cases of electron transfer involving oxygen will be illustrated.

2. The basic features of the EPR technique

EPR has been applied to surface chemistry and catalysis for about 30 years to study a variety of paramagnetic species (i.e. with one or several unpaired electrons).

Several review articles [1–3] have been devoted to the applications of EPR to surface problems since 1960.

Particularly important to the surface chemist, the high sensitivity of the technique permits the study of low concentration of active sites. The fact that diamagnetic species are not observed is both a limitation and an advantage of the technique, since, although a limited type of species can be observed, many highly reactive paramagnetic intermediates can be studied without any spectroscopic interference.

A free electron has a spin angular momentum (or simply spin) **S** which, in a given direction, can only assume two values. The direction usually specified is the z direction, so that the z-component of the spin S_z can have exclusively the two values M_s=1/2 and M_s=−1/2 in $h/2\pi$ units. An electron carries a magnetic moment μ_s which is colinear and antiparallel to the spin itself and given by the expression

$$\mu_s = -g_e\mu_B\mathbf{S},$$

where g_e is the free electron g value (g_e=2.0023) and μ_B is the Bohr magneton (μ_B=9.27×10^{-21} erg gauss^{-1}.

The interaction energy of the electron magnetic moment with an external applied magnetic field is classically given by

$$E = -\mu_s.\mathbf{B},$$

where **B** is the magnetic flux density measured in Tesla (T) or in Gauss (1G, 1T=10^4).

In quantum mechanics, the μ vector is replaced by the corresponding operator leading to the following Hamiltonian, i.e. the energy operator:

$$H = g_e\mu_B\mathbf{B}.\mathbf{S}.$$

The energies corresponding to the allowed orientations of the spin are therefore E=(+1/2) $g_e\mu_B\mathbf{B}$ and the energy difference between these levels is: ΔE= $g_e\mu_B\mathbf{B}$.

The transition between the two Zeeman levels can be induced by irradiating the paramagnetic system with a suitable electromagnetic radiation provided its frequency ν fulfills the resonance condition:

$$h\nu = g_e\mu_B\mathbf{B}.$$

For magnetic fields usually employed in the laboratory, the radiation required belongs to the microwave region. The energetic scheme of the Zeeman levels and of the corresponding transition is reported in Fig. 1 as well as the adsorbtion line and its first derivative.

The energy adsorbtion necessary to promote electrons from the lower to the upper energy level represents the resonance signal.

When the unpaired electron belongs to a ''real'' chemical system, the g value is, in general, different from g_e, i.e., when the orbital angular momentum is different from zero. In this case, the spin is no longer exactly quantized along the direction of the external

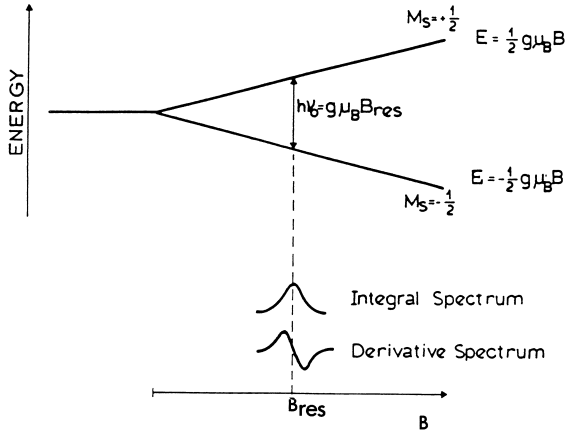

Fig. 1. The Zeeman energy levels of a free electron in an external applied magnetic field.

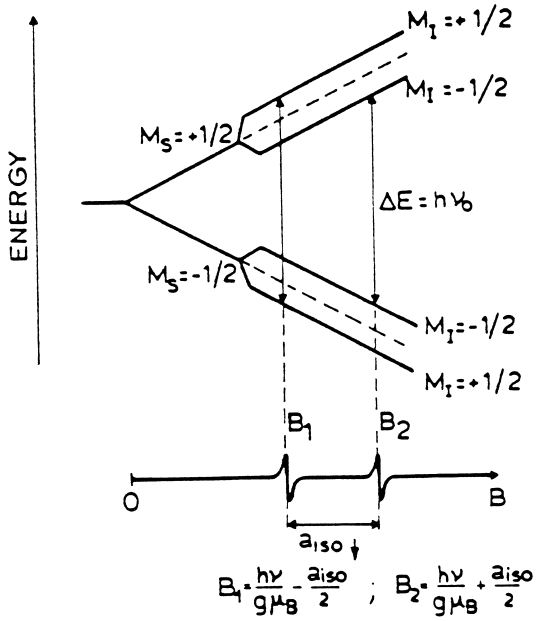

Fig. 2. Energy scheme of the levels produced by the interaction of an unpaired electron with a $I=1/2$ nucleus.

magnetic field, and, as shown below, the g value cannot be expressed by a scalar quantity but becames a tensor:

$$H = \mu_B \mathbf{B}\mathbf{g}\mathbf{S}$$

which is the new spin-Hamiltonian analogous to that reported before. The g_e (scalar) value in [3] is now replaced by **g**, a second rank tensor (or symmetric 3×3 matrix) representing the anisotropy of the interaction between the unpaired electron and the external magnetic field and outlining also the fact that the orbital contribution to the electronic magnetic moment may be different along different molecular axes.

Several nuclei possess spin and corresponding magnetic moments. The nuclear spin quantum number (I) of a given nucleus can assume integral or half-integral values in the range 0–6. The magnetic moment μ_n associated to a nucleus is collinear with the spin vector **I** according to the relation:

$$\mu_n = g_n \beta_n \boldsymbol{I},$$

where g_n is the nuclear g factor and β_n the nuclear magneton which is smaller than the Bohr magneton by a factor 1838, i.e., the ratio of the proton to electron mass.

When the paramagnetic center contains one or more nuclei with non-zero nuclear spin, the interaction between the unpaired electron and the nucleus with $I\neq0$ gives origin to further splitting of the Zeeman energies, and consequently, to the new transitions responsible of the so-called hyperfine structure of the EPR spectrum.

A typical hyperfine interaction is that observed for the hydrogen atom. The electron spin is interacting with the proton ($I=1/2$) spin. This latter may assume two possible orientations with $M_I=\pm1/2$. Thus the nuclear magnetic moment further splits each Zeeman level into sub-levels (Fig. 2) corresponding to two resonance lines.

More generally, in the case of n equivalent nuclei (i.e., *equally interacting* with the unpaired electron) having spin I, the EPR spectrum consists of $2nI+1$ lines which form the hyperfine structure.

Conversely, the knowledge of the number and separation of hyperfine structure leads to the number and the nature of interacting nuclei. The spacing between two consecutive lines is called the hyperfine constant. In general when one or more nuclei with $I\neq0$ are present in the system the whole hyperfine interaction is dependent on orientation and must be expressed by a tensor. The effective spin-Hamiltonian for an $S=1/2$ system containing j nuclei with $I\neq0$ thus

becomes:

$$H = \mu_B \mathbf{B} \mathbf{g} S + \sum_j \mathbf{I} \mathbf{A} \mathbf{S}$$

where **A** is the second rank hyperfine tensor.

The samples usually investigated by EPR in surface chemistry and catalysis are polycristalline materials, composed of numerous small crystallites randomly oriented in space. The resultant powder EPR spectrum is an envelope of spectra corresponding to all possible orientations of the paramagnetic species with respect to magnetic field: provided the resolution is adequate, the magnitude of the **g** and **A** tensor components can be extracted from powder spectra whereas no information can be obtained on the orientation of the tensor principal axes. The profile of the powder spectrum is determined by several parameters among which the symmetry of the **g** tensor, the actual values of its components, the line shape and the line width of the resonance.

These short introductory remarks are sufficient to understand the spectra reported in the following sections.

3. Routine measurements of the redox properties of surfaces

In many cases, a surface possesses redox sites whose nature, number and strength are often required to be known in order to understand their catalytic behavior. This has been made possible using charge transfer reactions involving solid–liquid or solid–gas systems. Charge transfer complexes are generally produced between the solid surface (S) and electron acceptor (A) or donor (D) organic molecules usually dissolved in benzene. The reactions can be written as

$$S + A \rightarrow S^+ + A^-$$

$$S + D \rightarrow S^- + D^+.$$

The ability of the surface to form radical ions depends on the ionization potential or on the electron affinity (IP and EA, respectively,) of the organic molecule. The threshold of IP or EA at which the charge transfer starts to be observed characterizes the strength of the sites whose number is given by the intensity of the paramagnetic signal of A^- or D^+. In this way the distribution of sites as a function of their strength can be determined. Typical molecules with low IP are perylene, anthracene, and naphtalene (π-bases) while high EA compounds which are commonly used are tetracyanoethylene, dinitrobenzene, trinitrobenzene, etc.

Electron transfer studies have been conducted on a wide range of acid or basic catalysts. Lunsford [2] and Flockhart [4] have reviewed the subject while Loktev and Slinkin [5] published a survey in the particular case of zeolites. The mechanism of formation of A^- and D^+ is still not very clear but the implications in catalysis are important: the correlation between redox sites and catalytic activities has been the subject of active research [6,7].

4. Oxygen surface chemistry and oxidation catalysis

Many chemical compounds, and in particular, the great majority of organic substances are thermodinamically unstable with respect to oxygen. However, a small fraction only is able to react spontaneously with oxygen at room temperature or at moderately higher temperature because of the high activation energy of the oxidation which is connected in its turn to the high energy of the O–O chemical bond. A second reason for the high activation energy in non-catalytic oxidations is due to the fact that molecular oxygen in the ground state is a $^3\Sigma_g$ triplet state whose reactivity with organic molecules (which usually are in the singlet state) is limited by the spin conservation rule. The height of the activation barrier can be reduced either by activation of the oxygen molecule to the singlet state or, more commonly, by catalytic activation of both the organic substrate and the oxygen molecule. The most common activation pathway of dioxygen at oxidic surfaces involves stepwise reduction of the molecule with formation of different types of molecular or atomic negative ions. In several instances the reductive activation of molecular oxygen involves not only adsorbed states but also the incorporation of oxygen into the oxide crystal lattice.

The nature and properties of oxygen species adsorbed on surfaces have been reviewed by Che and Tench in two review papers [8,9] where it is shown that most of these species are negatively

charged and are often bonded to the surface by ionic interaction even though, in some instances, a certain degree of covalency exists.

The most common negative species formed at the surface of oxides is the superoxide radical ion O_2^- The enthalpy of formation of superoxide in the gas phase (or, in other words, the electron affinity of oxygen) is negative (−42.5 KJ/mol corresponding to 0.44 eV) whereas all other negative oxygen species (in particular O^- and O_2^{-}) are unstable in the gas phase. All ionic species, however, may be stabilized by the Madelung potential at the surface of the oxide.

The activation of molecular oxygen is, in some instance, a complex process ending with the incorporation of the oxygen itself into the lattice of the solid oxide (vide infra). It is generally accepted that this process occurs stepwise according to the following scheme:

$$O_{2(g)} + e^- \rightarrow O^-_{2\,(surf)}$$

$$O^-_{2\,(surf)} + e^- \rightarrow 2O^-_{(surf)}$$

$$O^-_{(surf)} + e^- \rightarrow O^{2-}(s)$$

.

The direct transformation of the superoxide into O^-, as indicated in the scheme, seems more probable than the formation of a peroxide ion intermediate.

4.1. The superoxide ion adsorbed on surfaces

The O_2^- radical anion is, as stated before, the most stable oxygen anionic species in the gas phase. From Fig. 3, that reports the electronic configuration of the

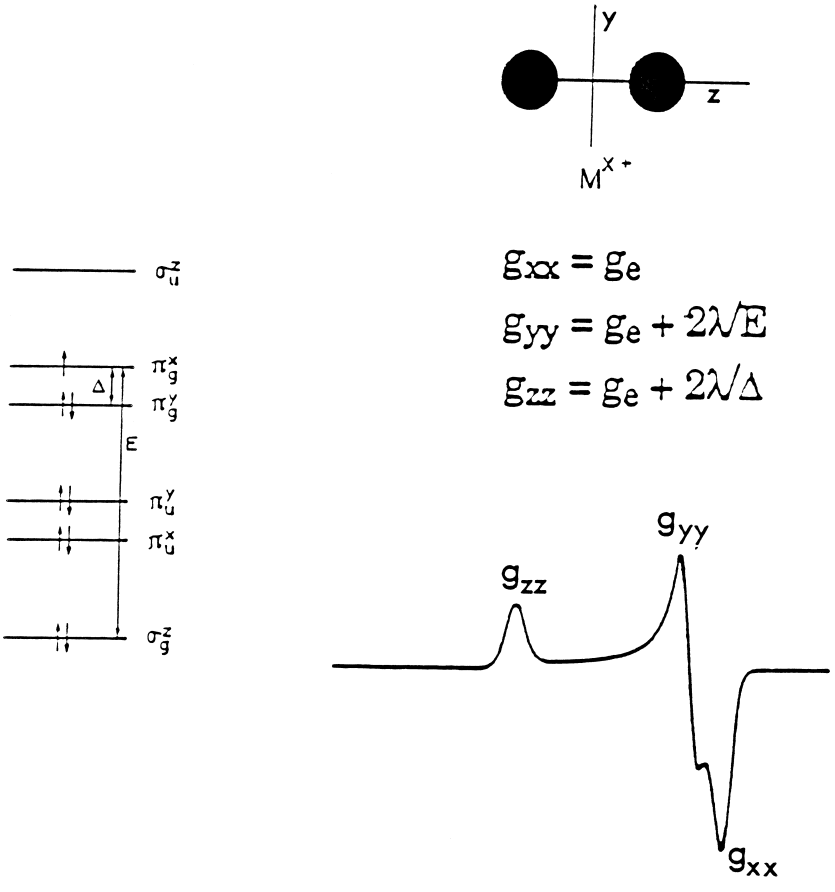

Fig. 3. Electronic configuration, g values and model EPR spectrum for adsorbed O_2^-.

species, it results that superoxide is a paramagnetic ion and that, therefore, EPR can be usefully employed to characterize its features.

Based on analysis of the EPR signal (and of its hyperfine and superhyperfine structures, if present) a wealth of information concerning the properties of the species could be obtained including identification of the surface adsorbing site, concentration, type of bonding and geometry.

In most cases of O_2^- formation at the surface of ionic oxides a purely ionic model was adopted to calculate the values of the g tensor elements. The formulas derived by Känzig and Cohen [9] on the basis of the ionic model are reported in Fig. 3 where the meaning of Δ and E is also defined. The symbol λ indicates the spin–orbit coupling constant of the oxygen atom. The figure also reports an example of EPR experimental spectrum due to superoxide ions. The most interesting of the g values is the g_{zz} one since it exhibits the greatest variance. The value of the g_{zz} parameter depends in fact on Δ which, in its turn, depends on the intensity of the crystal field exerted by the adsorbing center. Parameters such as the cation charge q, the charge/radius ratio and the distance between the superoxide and the adsorbing centers contribute to determine the value of g_{zz} whose measure is fundamental to identify the adsorption site.

4.2. *The O^- ion adsorbed on surfaces*

An O^- radical, either in the bulk or at the surface of an oxide, can be identified by determining the g and hyperfine tensors. In axial systems (quite often found in surface chemistry) the g values are given by:

$$g_{zz} = g_e, \qquad g_{xx} = g_{yy} = g_e + 2\lambda/\Delta E,$$

where ΔE is the energy difference between p_z (the orbital hosting the unpaired electron) and the two degenerate p_x and p_y orbitals. The direct observation of this ion by EPR is less common than that of superoxide in that its formation usually occurs at high temperature by further reduction of superoxide. Examples of O^- ions stable at room temperature have been obtained on both simple and mixed oxides by decomposition of N_2O. Stable O^- have also been observed in the Li_2O/MgO systems active in methane dimerization where they are formed and stabilized for reasons of charge compensation.

4.3. *Oxygen and catalytic oxidation*

As pointed out by Haber [10] catalytic oxidation reactions can be divided into two categories which are: (i) electrophilic oxidation occurring via activation of the oxygen molecule and (ii) nucleophilic oxidation in which the (usually organic) substrate is activated first, followed by insertion of nucleophilic oxygen (vide infra) in the substrate and hydrogen abstraction.

The two activated oxygen forms described before (the superoxide O_2^- and the O^- radical ions) are strong electrophilic reactants which attack the substrate molecule in the region of highest electron density (for instance a π bond). Unstable peroxy and epoxy intermediates are formed which lead to degradation of the carbon skeleton with carbon–carbon bond cleavage and eventually to the *total oxidation* of the substrate.

A second route of catalytic oxidation is the reaction with O_2^- lattice oxide ions which are nucleophilic and can be inserted, by nucleophilic addition, into an organic substrate previously activated on a suitable surface site. The first part of the catalytic cycle involves several successive steps of hydrogen abstraction and nucleophilic oxygen addition and ends with the desorption of the oxygenated product and with the simultaneous formation of oxygen vacancies and reduced cations on the solid. Such vacancies are then filled with oxygen from the gas phase. The oxygen reduction and incorporation into the lattice (which restores the initial redox state of the catalyst) do not necessarily take place at the same site from which surface oxygen is inserted into the substrate. This type of oxidation is called *selective oxidation* and the described mechanism is schematically reported Fig. 4. This mechanism was first proposed in 1950s

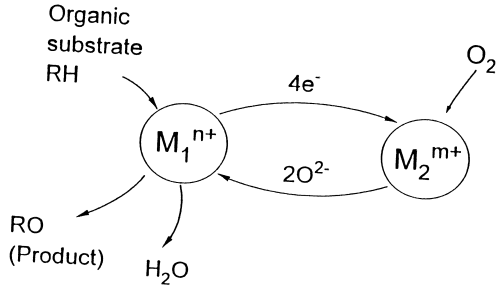

Fig. 4. The dual site mechanism in selective oxidation.

for the selective oxidation of aromatics by Mars and van Krevelen. A good candidate to catalyze selective oxidation reactions is an oxide with a certain propensity to loose oxygen and with good qualities of electron conductivity to ensure efficiency to the described redox process.

5. Electron transfer reactions leading to the formation of surface adsorbed superoxide

As discussed in the previous sections the main oxygen species adsorbed on an oxide surface at temperature lower than that of the catalytic reaction is the superoxide radical ion. The existence of peroxide ions has never been proved except in the case, not discussed here, of oxidation by H_2O_2. Some examples concerning the activation of O_2 in the form of superoxide on various solid systems are discussed in the following, considering different types of metal oxides.

5.1. Insulators

Typical examples of insulators are non-transition oxides like alkali-earth oxides, SiO_2, Al_2O_3. On such a kind of solids the existence of a wide band gap between the valence band and the (empty) conduction band (around 8–9 eV) severely limits the possibility of direct electron transfer to adsorbed oxygen. This is because the energy of the adsorbed species (a localized surface state) is higher than that of the electrons in the solid. The properties of an insulating oxide like MgO, however, can be modified in several ways.

A first method consists in generating electron donor centers in the solid. It is known since the early 1960s that exposure of some oxide to highly energetic irradiation generate defects consisting in electron trapped in anionic vacancies also called *F* centers or colour centers. Such centers can also be generated by addition of a low ionisation energy metal to the solid, and if the addition is performed at a reasonably moderate temperature (from RT to 600 K), the centers are localized at the solid surface [11,12]. In Fig. 5(a) the EPR spectra of a series of MgO samples containing *F* centers prepared by addiction of four different alkali metals are shown. The centers giving rise to the reported spectra are one-electron centers but two-electrons diamagnetic centers are also present. These

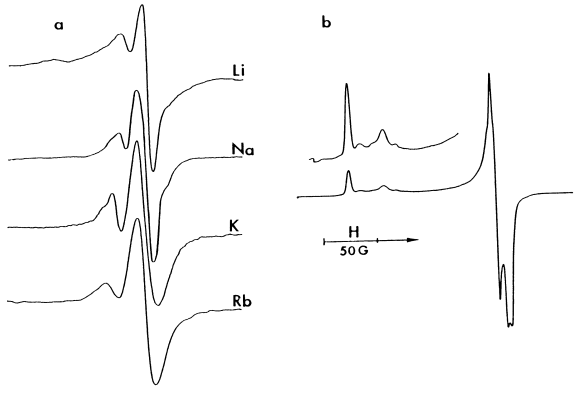

Fig. 5. EPR spectra of: (a) *F* centers on Me/MgO, (b) O_2^- formed by O_2 adorption on Me/MgO.

surface color centers are unstable towards oxygen and O_2^- radical ions are promptly formed by oxygen adsorption at low temperature. Recent quantum mechanical calculations [13] have shown that the electronic state corresponding to *F* centers lies in the band gap of the oxide. The electron transfer to oxygen occurs due to the contribution of both the electron affinity of oxygen and the Madelung stabilization of the adsorbed anion on positive centers at the surface. This latter contribution is by far the larger one. Fig. 5(b) reports the spectrum of O_2^- generated by contact of oxygen with the surface of MgO previously treated with metal sodium. The described systems are active as *superbasic catalytsts*.

5.2. Transition metal doped insulating oxides

A different method to modify the electron transfer properties of an insulator such as MgO consists in introducing a transition metal ion in the framework of the oxide. This, again, corresponds to modify the band spectrum of the solid with the formation of new electronic states. Interesting results have been obtained by doping MgO with Co^{2+} ions due to the solubility of the two oxides (MgO and CoO) in the whole range of molar concentrations. The MgO–CoO solid solutions directly adsorb oxygen giving rise, according to the adsorption temperature, to different EPR spectra. The two species stable at 77 K (I and II) are transformed at about 120–140 K in two other species (III and IV) which are stable up to room temperature. Species I–III are oxygen species

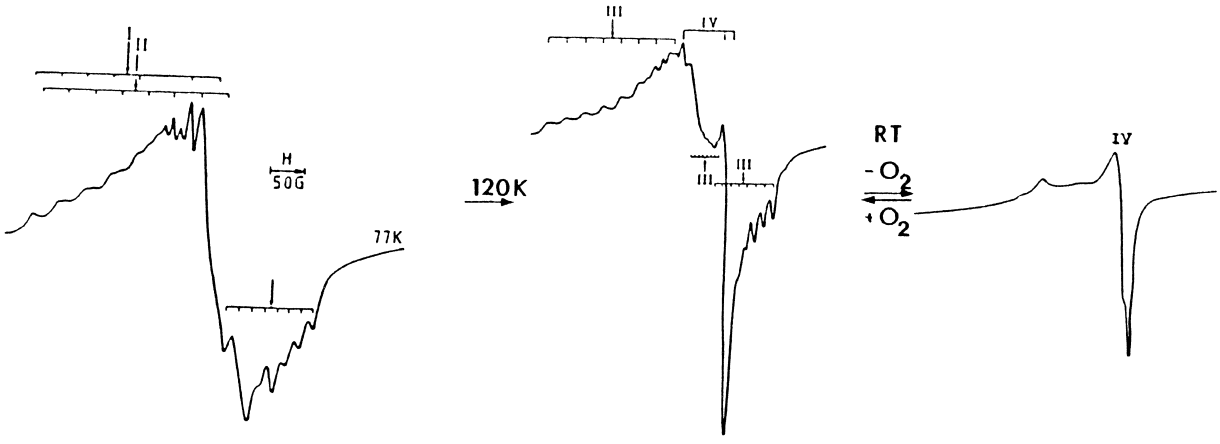

Fig. 6. EPR spectra of oxygen species on CoO–MgO (see text).

stabilized onto cobalt ions as shown by the complex superhyperfine structure due to interaction between the unpaired electron and the ^{59}Co nucleus (nuclear spin $I=7/2$, multiplicity=8 lines) and their nature can be roughly indicated as $Co^{3+}O^{2-}$ [14,15]. Fig. 6 illustrate the described reactions.

The most noticeable feature of species III is that it disappears upon evacuation at room temperature releasing molecular oxygen and leaving species IV only at the surface. Species IV is a "classic" superoxide on Mg^{2+} formed by spillover of O^{2-} from less stable cobalt adducts. Readmission of oxygen restores the cobalt–oxygen adduct (species III in Fig. 6). This reversible adsorption of oxygen indicates that a fraction, at least, of the surface cobalt centers behaves as oxygen carriers exactly like those iron or cobalt ion present in natural and synthetic molecules capable of oxygen transport. The CoO/MgO system is the first example of an *heterogeneous* oxygen carrier. The reaction pathway above illustrated is schematized in Fig. 7 that also reports the schemes of the surface site and of the cobalt–oxygen adducts. The basic reason of this unique property of the CoO/MgO surface is that the symmetry of the Co^{2+} coordination environment (C_{4v}) reproduces that of the molecular analogs mentioned above [14].

5.3. Semiconducting oxides

The electron transfer towards oxygen for semiconducting oxides is, in comparison with the case of insulators, an easier process which is related to the presence in the solid of suitable electron donor centers. The role of donor centers can be played by different lattice defects present in the surface layer essentially connected with deviation from the stoichiometry. In an *n*-type semiconductor, for instance, the donor centers are occupied electron levels in the band gap region quite close to the conduction band, and the Fermi level of the solid is between the donor levels and the conduction band itself.(Fig. 8(a)). The electron transfer from the solid to oxygen, which forms the surface acceptor level, is easy if the energy of this latter one is below the Fermi level of the solid. The contribution of the electrostatic stabilization of the anionic species on the surface can play, like in the case illustrated in the previous section a fundamental role in determining the energy of the adsorbed species. The electron transfer towards an adsorbate causes, in the case of *n*-type semiconductors, a decrease of the electron population in the donor level near the conduction band and a consequent decrease of the solid conductivity. Furthermore, since the electrons are initially transferred to the surface from isolated centers present in the surface and subsurface layers, in this spatial region of the solid a positive charge develops forming, with the negative charge of the adsorbed species, an electrical double layer [16]. This causes the increase of the electrical work function or, in other words, generates an energy barrier (Schottky barrier) that increases with progressive electron transfer limiting therefore the electron transfer itself (depletive

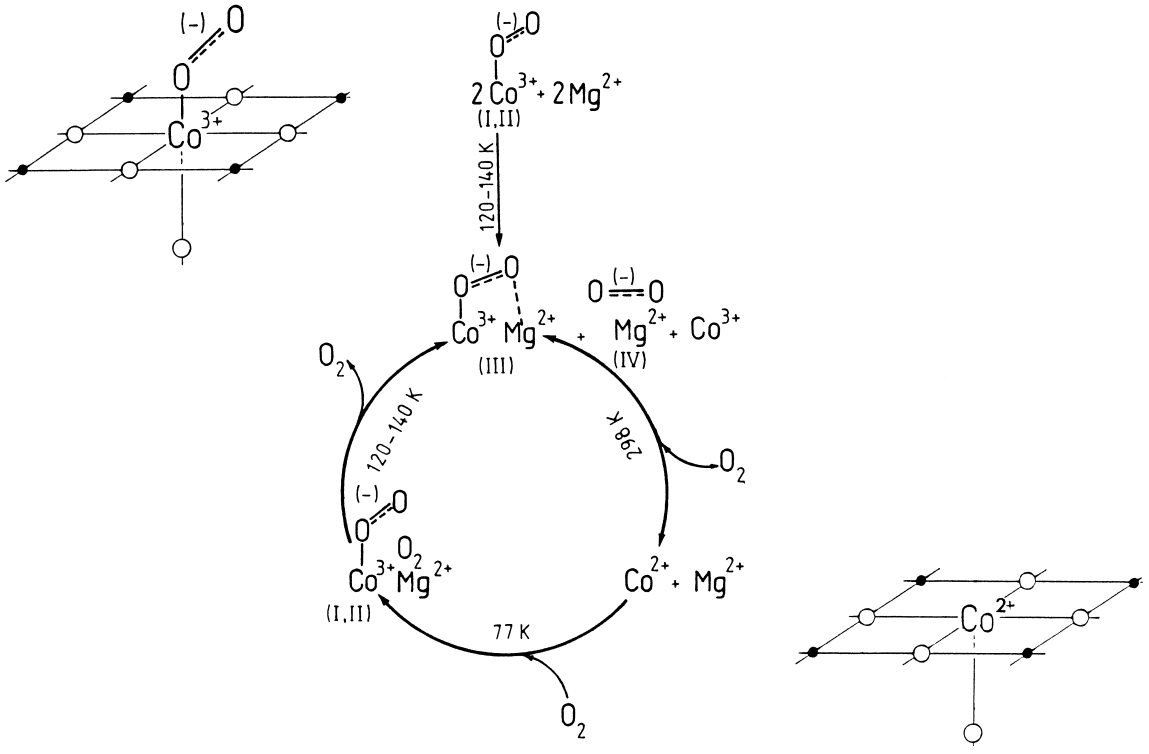

Fig. 7. Pathway of the interaction of oxygen with a (CoO/Mg) surface

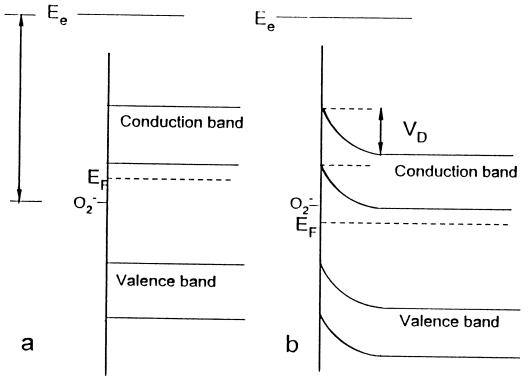

Fig. 8. Energy of the bands in an *n*-type semiconductor before (a) and after (b) adsorption of oxygen in the form of superoxide anion.

adsorption). In terms of energy band schemes this can be seen as a bending of the bands of the solid with consequent decrease of the energy difference between the level of the surface adsorbed oxygen and the Fermi level of the solid (Fig. 8(b)). The behavior of a *p*-type semiconductor, in the case of adsorption of negative oxygen species, is, of course, opposite to that described for *n*-type ones and no limitation to the electron transfer arises.

5.4. Surface intermolecular electron transfer

Although the formation of O_2^- at the surface of an insulating oxide by direct electron transfer is blocked by the high energy gap it has been shown that several hydrocarbons (propene and toluene for instance) undergo oxidation in mild conditions at the surface of MgO which lead to the cleavage of the molecule. In the case of propene, for instance, the contact with oxygen at the surface of MgO causes the formation of adsorbed acetates, formates and carbonates at ambient temperature and the total oxidation at higher temperature. This fact is the finger print of an electrophilic oxidation responsible of which must be a superoxide or an O^- species (see Section 4). Superoxide O_2^- ions were indeed observed at the surface of deeply out-

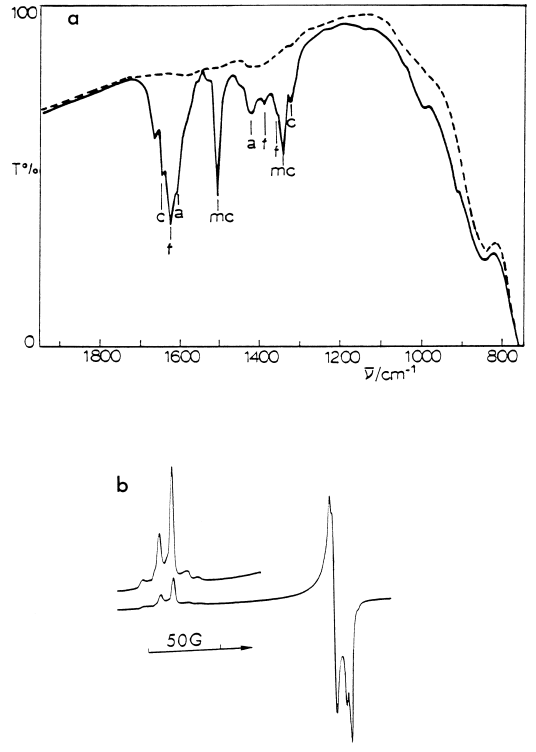

Fig. 9. Infrared and EPR spectra of superoxide ions recorded upon propene–oxygen interaction on MgO. The letters "a" "c" and "f" stand for acetates, carbonates and formates, respectively.

gassed MgO in the presence of hydrocarbon–oxygen mixtures. This fact is not, however, in contradiction with the insulating nature of the oxide discussed above and has been interpreted introducing the concept of surface intermolecular electron transfer [17–20]. The fundamental factor that determines the observed reactivity is the basic nature of the MgO surface. Surface oxide O_2^- ions, in fact, are able to eterolitically split the hydrocarbon molecule forming a proton (readily stabilized at the surface in the form of OH^-) and a carbanion:

$$R - H + O^{2-}_{(surf)} \rightarrow OH^-_{(surf)} + R^-_{(ads)}$$

The carbanion is unstable towards molecular oxygen and readily transfer an electron to the oxygen itself:

$$R^-_{(ads)} + O_{2(g)} \rightarrow O^-_{2\,(ads)} + R^{\bullet}$$

The superoxide ions (a fraction of which is captured by low coordination ions at the surface and becomes EPR visible) then react, probably in their protonated form HO_2, with the *R* radical:

$$OH^-_{(surf)} + O^-_{2\,(ads)} \rightarrow HO_2 + O^{2-}_{(surf)}$$

$$HO_2 + R \rightarrow ROOH$$

The peroxo species given rise may decompose in more than one way leading to the cleavage of the molecule and the formation of oxidized products. In the specific case of propene one has

$$CH_2{=}CH\text{-}CH_2OOH \quad \begin{array}{c} CH_3\text{-}CH - CH_2 \\ \backslash \quad / \\ O\text{-}O \end{array} \quad CH_3CHO + HCHO$$

with formation (at RT) of surface adsorbed acetates and formates (Fig. 9). Such a mechanism shows how a deep oxidation involving electrophilic reduced oxygen species can take place without direct activation of molecular oxygen by electron transfer from the solid. In this case the driving force of the process is uniquely the basic strength of the oxide ions at the surface.

6. Conclusions

In the present contribution the importance of surface oxygen radical species (formed by electron transfer processes) in catalytic oxidation reactions has been illustrated. The role of EPR in this kind of research and the basic information on the oxygen species derived by EPR investigation have been also discussed. The various process of electron transfer to oxygen have been discussed as a function of the conductivity properties of the various oxides.

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