On the Role and Applications of Electron Magnetic Resonance Techniques in Surface Chemistry and Heterogeneous Catalysis

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Abstract
Some relevant aspects of Electron Paramagnetic Resonance (EPR) applied to the fields of surface chemistry and heterogeneous catalysis are illustrated in this perspective paper that aims to show the potential of these techniques in describing critical features of surface structures and reactivity. Selected examples are employed covering distinct aspects of catalytic science from morphological analysis of surfaces to detailed descriptions of chemical bonding and catalytic sites topology. In conclusions the pros and cons related to the acquisition of EPR instrumentations in an advanced laboratory of surface chemistry and heterogeneous catalysis are briefly considered.

Graphic Abstract

Keywords Electron magnetic resonance · Heterogeneous catalysis · Surface chemistry · Catalysis, oxide supports · Zeolites · Ziegler–Natta

1 Introduction
Electron Paramagnetic Resonance, EPR, has been employed in experimental research on surface chemistry and heterogeneous catalysis since the beginning of the sixties. This technique, after the first experiment performed by E. Zavoisky’s in USSR in 1944, was independently developed in the same period in Oxford by B. Bleaney and a group of theoretical physicists (Abragam, Pryce) who laid the foundations of the discipline. The first applications of the EPR technique were devoted to the properties of transition metal ions compounds and those of paramagnetic defects in the solid state. The important achievements in these two research areas combined with the sensitivity of the technique and the unique level of detail in the description of those features of

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the electron wave function related to the unpaired electron
distribution, stimulated the application of the technique to
the study of surface chemistry and heterogeneous catalysts.

The first review article concerning applications of EPR
to heterogeneous catalysis dates back to 1960 [1] and is
relatively poor of experimental data. Much more results
are found in review papers intermittently appeared later
[2–11] and describing the growing role of EPR in char-
acterizing systems of interest for heterogeneous catalysis
such as adsorbed paramagnetic molecules, surface defects
centres, surface reaction intermediates and supported tran-
sition metal ions. Recently, beside the classic EPR acro-
nym, the broader Electron Magnetic Resonance (EMR) one
has been introduced that includes a variety of experimental
approaches involving the interactions of electron magnetic
dipoles with an external magnetic field. Both acronyms will
be used in the present article that has been written with the
aim of answering two elementary questions. The former one
is: what are the main aspects of surface chemistry and het-
erogeneous catalysis that can conveniently be investigated by
electron magnetic resonance techniques? The second one is:
what are the potential advantages (and the disadvantages) for
a research group in these disciplines that intends to invest in
an EPR instrumentation? The answer to the former question
will be provided using a number of specific examples mainly
derived from the experience of our group and covering dis-
tinct areas the catalytic sciences.

The paper is organized as follows. In the first part, the
principles of the EPR technique will be concisely described,
referring to specific contributions available in the literature
for more in-depth treatments. In the central part, some top-
ics of surface chemistry and catalysis will be illustrated
through specific examples showing the capability of EPR to
play an important role in the advancement of knowledge. In
conclusion, the advantages of EMR and the disadvantages,
that inevitably limit an even more widespread use of these
techniques, will be briefly discussed.

2 Basic Features of Electron Magnetic
Resonance

The conventional continuous wave (CW) EPR is, among
the various EMR techniques, the dominant one in hetero-
geneous catalysis studies. The distinctive feature of EPR
is that it exclusively monitors paramagnetic species i.e.
chemical entities bearing one or more unpaired electrons
and is blind to all diamagnetic entities. This is a clear dis-
advantage in view of a broad application of the technique
but this selectivity can also be thought as an advantage,
considering that a given paramagnetic center belonging
to a complex chemical system (e.g. a paramagnetic ion
in a protein or dispersed in a zeolitic framework) can be
studied without any interference. Clearly, care must be
taken to make sure that the active paramagnetic species is
also a catalytically relevant species. To be complete it has
also to be taken in mind that, in some particular instances,
there are paramagnetic species escaping EPR detection,
because of mutual physical interactions due to their close
proximity.

Electron magnetic resonance occurs when an electromag-
netic wave of suitable frequency (usually in the microwave
region) interacts with the sample immersed in an applied
magnetic field and causes the inversion of the spin (and thus
of the magnetic moment) of the unpaired electrons so that a
certain amount of electromagnetic energy is absorbed by the
system. Considering a free electron, the effect of an applied
magnetic field \( B \) is to generate two distinct spin states (Zee-
man effect). The electrons in the lower state (\( \beta \)) can be pro-
moted in the upper state (\( \alpha \)) by absorption of a quantum of
electromagnetic radiation energy, \( h\nu \), coinciding with the
energy difference between the two states

\[
h\nu = g \mu_B B
\]  

where \( \nu \) is the radiation frequency, \( g = 2.0023 \) the free elec-
tron \( g \) value and \( \mu_B \) a constant called the Bohr magneton.
The EPR spectra are usually reported, for technical reasons,
as the first derivative of the microwave absorption as a func-
tion of the swept magnetic field. The most commonly used
microwave frequency in the study of heterogeneous catal-
ysts and photocatalysts is ca. 9.5 GHz in the range of the
so called X-band, 8–12 GHz, the most often used in radar
applications. In this case the magnetic induction necessary
to observe the resonance of a free electron or of a simple
organic radical falls around 350 mT. Other regions of micro-
wave frequencies used in commercial EPR spectrometers are
Q-band (around 35 GHz) and W-band (95 GHz). Continu-
ous wave techniques include CW-EPR, ENDOR (Electron
Nuclear Double Resonance) and HF-EPR (High Field EPR).

Similarly to what was done in Nuclear Magnetic Reso-
nance, pulsed methods were also introduced in EPR, though
more recently. The reason why the development of commer-
cial pulse EPR spectrometers lagged behind that of NMR is
related to the much faster electron relaxation times, which
are of the order of \( 10^6 \) times faster than those of nuclei,
requiring pulse timings \( \approx 10^6 \) times shorter for pulsed
EPR than for pulsed NMR. This fact not only slowed down
the evolution of commercial pulse EPR spectrometers with
respect to NMR but poses some limit to the application of
pulse EPR techniques especially in catalytic systems featur-
ing the presence of nanoparticles or high spin states. On the
other hand, when applicable, the selectivity and resolution
of pulse EPR experiments, in particular of so called hyper-
fine techniques of ENDOR and ESEEM (Electron Spin Echo
Envelope Modulation), can provide sub-MHz resolution,
allowing to couple the sensitivity and selectivity of EPR with the resolution of NMR. Under such circumstances coordination spheres up to the third can be investigated.

The EPR spectrum of a paramagnetic species is the result of a series of interactions of the unpaired electron(s) with the surroundings and it can be described in terms of a spin Hamiltonian, that is a series of energy terms each one corresponding to a distinct interaction. For the purposes of the present paper it is sufficient to consider the following three terms of the spin-Hamiltonian.

\[ H = \mu_B S \cdot B + S \cdot A \cdot I + S \cdot D \cdot S \]  

(2)

The first term (electronic Zeeman operator) accounts for the interaction of the electron spin \( S \) with the external magnetic field \( B \). The interaction is determined by the \( g \) tensor, a \( 3 \times 3 \) matrix which, in general, can be reduced to its diagonal form. The tensorial nature of the \( g \) tensor indicates that the resonant magnetic field varies according to the orientation of the paramagnetic species in the magnetic field itself. The values of the diagonal elements of the \( g \) tensor (that are somehow equivalent to the chemical shift in NMR) depend on the electronic structure (ground and excited states) of the paramagnetic species.

The second term represents the interaction between electron spin and nuclear spins (hyperfine interaction, hpf). \( A \) is the hyperfine tensor and \( I \) is the nuclear spin vector. In CW-EPR the hyperfine interaction gives rise to the so called hyperfine structure. A set of \( 2I + 1 \) lines is expected (for any given orientation of the species into the magnetic field) for the interaction of the electron spin with a nucleus having non-zero nuclear spin (quantum number \( I \neq 0 \)). \( A \) is composed of two main contributions, i.e. the isotropic Fermi contact term \( A_{\text{iso}} \) (a scalar related to electron spin density in the volume of the nucleus observed for s-type orbitals only) and the anisotropic electron-nucleus dipolar coupling expressed by a matrix \( T \). The term hyperfine interaction is typically associated to the interaction between the unpaired electron of a given species and the nuclei belonging to the species itself. The same type of interaction, when it involves magnetic nuclei of entities surrounding the magnetic centre (such as the ligands in the case of a coordination compound) is sometimes referred to as super-hyperfine (shf) interaction.

The third term describes the interaction between two or more unpaired electrons (\( S > 1/2 \)) which is gauged by the \( D \) tensor. Systems with \( S > 1/2 \) are frequent in the case of transition metal ions. Ions such as Fe\(^{3+} \) or Mn\(^{2+} \) in high spin configuration, for instance, are characterized by \( S = 5/2 \). The \( D \) tensor can be expressed in terms of two quantities (\( D \) and \( E \)) that account for the “zero-field splitting”, the interaction between unpaired electrons occurring in the absence of the external magnetic field.

The tensors present in all terms of Eq. 1 reflect the anisotropy of magnetic interactions. This means that, when the paramagnetic system is located in a single crystal, the EPR signal changes according to the orientation of the crystal in the external magnetic field \( B \). A careful measure of all the magnetic tensor components is obtained, in this case, recording the EPR spectrum at various orientations of the crystal axes in the applied magnetic field.

Single crystals have been employed in EPR studies of surface science and catalysis in few cases only. Much more common, in particular in the case of real heterogeneous catalysts, are disordered systems e.g. polycrystalline materials (or powders) composed by many crystallites casually oriented in space. In this case the shape of the “powder spectrum” does not vary with the orientation of the sample in the external field and contains, in principle, all the information about the magnetic tensors in Eq. 1. The EPR powder spectrum is the envelope of single spectra corresponding to all possible orientations of the paramagnetic species with respect to the applied magnetic field. The presence of resonance in a range of magnetic field (say, \( B_{\text{min}} - B_{\text{max}} \)) does not create, however, a uniform envelope. The microwave absorption reported as a function of the resonant field \( B_{\text{res}} \) has turning points for orientations corresponding to the principal (or diagonal) components of the \( g \) tensor which show up in the first derivative spectral trace. Figure 1 shows three examples of powder spectra. In the first two cases there is no hyperfine interaction (\( I = 0 \)) and the information is limited to the only \( g \) tensor which is axial in the first case (Fig. 1a, \( g_{xx} = g_{yy} = g_\perp \)), and rhombic in the second one (Fig. 1b, \( g_{zz} \neq g_{xx} \neq g_{yy} \)). In Fig. 1c the \( g \) tensor in the same of Fig. 1b but

**Fig. 1** Calculated spectral profiles of the EPR powder spectra (first derivative of absorption as a function of the swept magnetic field) in the case of an axial \( g \) tensor (a) and a rhombic \( g \) tensor in the absence of hyperfine interactions (b). The profile in (c) is based on the \( g \) tensor of the species in (b) with the onset of a hyperfine interaction with a nucleus having \( I = 3/2 \) (four lines)
the three principal components are split in four lines due to hyperfine interaction with a nucleus having \( I = \frac{3}{2} \).

It should be outlined that all cases in Fig. 1 report a signal related to a single paramagnetic species containing information on the three principal values of the \( g \) tensor. It is thus mistaken to treat (as unfortunately it can be found in some examples present in the literature) the various \( g \) components as independent features corresponding to distinct species.

Determining the exact \( g \) and \( A \) values in real cases can be difficult. This is due to several factors such as: (i) the presence of more than one species with overlapping signals (the range of the observed \( g \) values is relatively limited for a large fraction of the more common paramagnetic species), (ii) poor resolution of the hyperfine structure, (iii) line broadening due to magnetic interactions between nearby species. For this reason it is often necessary, for an unambiguous assignment of the spectra, the use of tools such as multifrequency EPR (recording spectra at more than one frequency) and isotopic substitution (inserting atoms with different nuclear spin in the paramagnetic species or in its surroundings). Furthermore, the computer simulation of the experimental spectra is an essential good practice to verify and to refine the set of spin-Hamiltonian parameters derived from a preliminary analysis of the spectrum and, in the recurrent case of the simultaneous presence of various paramagnetic species, to evaluate the abundance of each of them.

Among the above mentioned pulse-EPR techniques, particular emphasis, in this paper, will be given to HYSCORE (Hyperfine Sublevel Correlation spectroscopy). This is a two dimensional technique based on a particular pulse sequence that creates a correlation between the nuclear frequencies in the two spin manifolds allowing the observation of NMR transitions related to nuclei in the surroundings of the paramagnetic centre. An HYSCORE experiment, similarly to the ENDOR experiment, is particularly appropriate to measure weak hyperfine interactions undetectable by CW-EPR, which can however be very revealing of the coordination environment and catalytic function of paramagnetic species. A review on the advantages of high field ENDOR in the characterization of functional sites in microporous materials can be found in ref. [12], while some case studies are reported in ref [13–16]. Several comprehensive textbooks are available for the reader interested to a deeper knowledge of the physical bases of electron magnetic resonance and of the mentioned advanced techniques [17–22].

### 3 EPR in Surface Chemistry and Catalysis

A classic CW-EPR spectrometer is built up to allow the interaction of microwaves having a fixed frequency with a sample kept into the lines of force of a variable magnetic field. In short, the technical apparatus is based on a microwave bridge that generates microwaves which are sent through a wave-guide to a resonant cavity containing the sample and capable to store the microwave energy. The cavity is placed into a homogeneous magnetic field produced by an electromagnet. Despite the size and weight of this experimental apparatus the EPR technique can be adapted to the complex experiments required in catalytic research. The experiments, in fact, can be run in a wide range of temperature. The very low values of liquefied helium (from about 4 K onwards) or nitrogen (from 77 K) are employed to obtain resolved, low-linewidth spectra while the high temperatures typical of real catalytic processes are used in the so called EPR in-operando (see below). The resonant cavity also contains a window that allows the illumination of the sample with light in the range between UV and IR. This allows unique opportunities in the field of photocatalysis e.g. monitoring the excited states of the photocatalyst or following the state of the system during the photocatalytic reaction [23]. Another point in favor of the use of EPR in surface science and catalysis is the high sensitivity of the technique (the limit of detection corresponds to about \( 10^{12} \) spin) that allows monitoring low concentration intermediates typical of catalytic phenomena often undetectable by other techniques.

The main experimental issues potentially covered by EPR experiments in surface chemistry and catalysis can be summarized as follows:

- probing the morphological features of surface sites
- nature and properties of reactive surface intermediates
- unravelling the chemical bonding at solid surfaces
- topological description of active sites in catalytic systems
- geometrical and electronic structure of catalytic sites via selective isotopic enrichment
- catalytic sites under real conditions (operando EPR)

Specific examples on each item will be illustrated in the following of this paper except for the last one. The reader is referred, in this case, to exhaustive specific reports about EPR in operando that have been published along the years and illustrate in detail the particular feature of such an approach [10, 24–26]. Furthermore, the particular subject of EPR investigation in photocatalysis is mentioned in a Sect. 3.2.2. however not treated in great detail. A specific article on this topic has been recently published [27].

#### 3.1 Probing the Morphological Features of Surface Sites of Metal Oxides

In the Introduction, emphasis was put on the role of EPR in unravelling the features of paramagnetic systems. Actually a second, alternative approach in EPR research exists that is exploring the features of a diamagnetic system.
using a paramagnetic molecule acting as spin probe. This approach has been widely used in the investigation of soft
matter (membranes, micelles etc.) and it can be also applied
to solid surfaces, in particular of metal oxides, in order to
monitor the surface crystal fields and for surface sites iden-
tification. The most common spin probes employed in the
surface chemistry of metal oxides are the superoxide rad-
cal ion \((O_2^-)\) which has to be generated in some way by a
surface reaction or nitric oxide (NO) which, as opposite, can
be directly adsorbed on a bare surface.

NO is an 11-electron molecule with one electron in \(2\pi\)
degenerate antibonding orbitals and \(^3\Pi_{1/2}\) ground state. The
ability of this molecule as a surface probe is twofold in that
it can reveal both the surface crystal field of cationic sites
and the presence of highly basic \(O_2^-\) oxide ions.

In the former case NO acts as a probe when physisorbed
at low temperature [28]. In such conditions the electric field
present at the surface of the ionic crystal in correspond-
ence of specific cationic sites splits the energies of the \(2\pi\)
antibonding orbitals by a factor \(\Delta\). The EPR spectrum of
nitric oxide is based on an orthorhombic \(g\) tensor whose \(g_{zz}\)
component (\(z\) is the direction corresponding to the molecular
axis) directly depends on \(\Delta\) according to the following, first-
order approximated, equation

\[
g_{zz} = g_e - \frac{2\lambda}{\Delta} \tag{3}
\]

The \(g_{zz}\) component thus becomes a measure of the elec-
tric field felt by the adsorbed nitric oxide (NO).

The EPR spectrum of nitric oxide physisorbed on poly-
crystalline MgO is reported in Fig. 2.

\[
MgO is a highly ionic basic oxide exhibiting the simple
structure of sodium chloride. The coordination 6 of bulk
ions reduces to 5, 4 or 3 when the ions are exposed at the
surface. Due to its relatively simple features MgO has served
has as a model system for the investigations of both surface
science [29] and surface chemistry [30] of metal oxides. By
the way, a quite spectacular example of the the success of
EPR in providing atomistic information of the structure of
reactive sites at surfaces indeed concerns this oxide. This
is the case of the so-called \(F_s^+\) sites that for a long time were
described in terms of oxygen vacancies containing unpaired
electrons. However, thanks to high resolution EPR experi-
ments coupled with DFT calculations it was shown that they
consist of electrons trapped at particular cationic sites where
they are stabilized by the joint action of surface cations and
nearby hydroxyl groups [31, 32]. This topic has been the
object of specific review papers [33] and will not be further
discussed here.

Going back to nitric oxide interaction with MgO, the main
features of the EPR spectrum of physisorbed NO is a N hyper-
fine triplet centered at about \(g = 1.99\) (\(^{14}\)N is the most abun-
dant—99.6%—nitrogen isotope and has nuclear spin \(I = 1\)).
The spectrum also exhibits, at higher field, three different
\(g_{zz}\) lines (\(g_{zz} = 1.9610, g_{zz} = 1.9188, g_{zz} = 1.8900\) which are
independent one from the other [34]. Each of these high field
lines is also split in three components by N hyperfine interac-
tion but the splitting is fully appreciable on the third line only
\(g_{zz} = 1.8900\)). The spectrum in Fig. 2 (top) has been therefore
interpreted in terms of the presence of three NO molecular
species weakly adsorbed on three distinct \(Mg^{2+}\) sites. The
adsorbed NO species differ essentially in the higher field \(g_{zz}\).
component (Δ splitting value) reflecting the different polarizing power, hence the Madelung potential of the surface sites. The lower \( g_{zz} \), the higher Δ (Eq. 3). The three surface sites monitored by NO have respectively coordination 5, 4 and 3 (scheme in Fig. 2) as also confirmed by theoretical modelling [34].

Nitric oxide, as a paramagnetic probe, can also be employed to identify the sites responsible of particular surface reactivity. This is the case, for instance, of the heterolytic dissociation of \( \text{H}_2 \) at the surface of MgO that is fully reversible at room temperature and has been widely investigated in the past. The EPR spectrum in Fig. 2 (bottom) has been recorded after the adsorption of a \( \text{H}_2-\text{NO} \) mixture. It is easy to see that this second spectrum, again due to adsorbed NO, shows the fingerprint of the 5-coordinated ions only (\( g_{zz} = 1.89 \)) firmly indicating that the two other families of low coordination sites (4-c and 3-c) are those involved in the dissociative chemisorption of the hydrogen molecule. The latter process selectively block the lower coordination sites that are no more available for the weak NO polarization [35].

NO is indeed a multitasking probe. In the case of basic oxides it can also probe highly basic \( \text{O}^2^- \) ions forming covalently bound \( \text{NO}^2^- \) adducts which are paramagnetic and have a typical EPR spectrum which can be observed at room temperature in the absence of physisorbed NO. These highly basic sites are a very minor fraction of surface MgO oxide ions but their amount increases moving to oxides with higher basicity such as CaO [36].

The NO molecule is also sensitive to the presence of transition metal ions at the surface due to their propensity to form nitrosyl adducts. An example is that of the interaction with a MgO matrix containing 1% of Ni\( ^{2+} \) homogeneously dispersed in the solid matrix (MgO and NiO have the same NaCl structure and are soluble in the whole range of concentrations). Probing the surface of this solid solutions by NO adsorption, the spectrum in Fig. 3 shows up. Remarkably NO is still capable to monitor the Mg\( ^{2+} \) surface sites (the signal at high field in Fig. 2 is the same discussed above) even though the spectrum is dominated by an intense axial signal at lower field. This has the structure with \( g_\| > g_\perp > g_e \) typical of the spectrum of 3\( d^9 \) ions and is due to Ni\( ^{3+} \) ions that forms by interaction of NO with Ni\( ^{2+} \) ions at the MgO terrace.

Such an interaction is essentially an electron transfer from the molecule to the surface ion that leads to the formation of an adduct schematically indicated as Ni\( ^{3+}\text{NO}^+ \) [37]. Theoretical calculations confirm this picture describing in detail the nature of this bent nitrosyl adduct (see Scheme in Fig. 3) which host the unpaired electron in the Ni\( d_{x^2-y^2} \) orbital.

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3.2 Nature and Properties of Reactive Surface Intermediates

3.2.1 Superoxide Intermediates in Oxidation of Alkenes on MgO and C–H Heterolytic Splitting

Catalytic materials based on metal oxides have a dominant role in heterogeneous catalysis and, in parallel, molecular oxygen is an important reactant in several catalytic processes. It is therefore understandable that oxygen species at the surface of oxides play a crucial role in many heterogeneous processes. The classic Mars–Van Krevelen mechanism for selective oxidation of hydrocarbons, for instance, epitomizes this concept since it involves the incorporation of gas phase oxygen into the bulk of the oxide catalyst that loses oxygen while oxidizing the organic substrate. Oxygen incorporation is thought to occur via a stepwise reduction involving the formation of various reactive intermediates some of which are paramagnetic.

\[
\begin{align*}
\text{O}_2(\text{g}) \rightarrow \text{O}_2^-_{\text{ads}} & \rightarrow \text{O}_2^{2-}_{\text{ads}} \rightarrow \text{O}_2^-_{\text{ads}} \rightarrow \text{O}_2^{2-}_{\text{surf}} \quad (4)
\end{align*}
\]

All species present in Eq. 4 are highly reactive and can be formed not only by reduction of molecular oxygen but also via different processes occurring at the surface. Two of them (\( \text{O}_2^- \) and \( \text{O}^- \)) are paramagnetic and may be monitored by EPR. We will refrain here to report details on the structure of the EPR spectra of these two species that are widely discussed elsewhere [38, 39], limiting ourselves to
shortly illustrate two examples with oxygen reactive species playing a key role in complex reaction mechanisms. As it will be shown the detection by EPR of these paramagnetic intermediates contributes to elucidate details of the mechanism itself.

The oxidation of alkenes in mild conditions on the surface of magnesium oxide was described years ago. In the case of propene, the reaction is initiated by the basic action of the surface $\text{O}^{2-}$ ions. These are able to heterolytically split the C–H bond abstracting a proton and forming the corresponding carbanion [40]

$$\text{C}_3\text{H}_5-\text{H} + \text{O}_2^{2-}_{\text{surf}} \rightarrow \text{C}_3\text{H}_5^{2-} + \text{OH}_\text{surf}^{-}$$ (5)

The surface adsorbed carbanion is unstable and in presence of oxygen an electron transfer occurs producing surface adsorbed superoxide ions (which can be monitored by EPR) and a reactive organic radical:

$$\text{C}_3\text{H}_5{(\text{ads})} + \text{O}_2{(\text{g})} \rightarrow \cdot\text{C}_3\text{H}_5 + \text{O}_2^{2-}$$ (6)

This mechanism, indicated as surface intermolecular electron transfer (SIET) [41] continues with formation of oxygenated compounds such as acetates, formates and carbonates. The kinetics is zero order with respect to propene and second order with respect to the adsorbed $\text{O}_2^{2-}$ intermediate with a typical Langmuir–Hinselwood mechanism [42]. The direct observation of adsorbed superoxide ions upon co-adsorption of a hydrocarbon and oxygen is therefore diagnostic of the presence of a basic sites capable of heterolytic splitting of C–H bonds having extremely low acidity (Eq. 5). Propene ($\text{pKa}=35$) is split at the surface of MgO while methane ($\text{pKa}=40$) is not. This ability typical of basic oxide ions increases moving from MgO to the other alkaliearth oxides. In the case of calcium oxide, the formation of superoxide has been observed for saturated hydrocarbons with acidity lower than that of propene ($\text{pKa}=40$).

Figure 4 reports the energy levels of an adsorbed superoxide. This is a 13e-π radical whose π antibonding degenerate orbitals are split by a factor $\Delta$ by the crystal field of the adsorbing cation. In analogy to what described for the NO molecule (Sect. 3.1) the z component of the $g$ tensor ($z$ is the O–O axis direction) is sensitive to this splitting being

$$g_{zz} = g_e + 2\lambda/\Delta$$ (7)

Notice that the formula is similar to that in Eq. (3), the inversion of the sign being due to the difference between the NO configuration (one electron in the 2π* orbitals) and that of $\text{O}_2^{2-}$ (one hole in the same orbitals). A schematic EPR signal of adsorbed superoxide is also shown in Fig. 4 top. The signal is rhombic with the $g_{yy}$ and $g_{xx}$ components quite close one to the other. Similar to the case of NO, $g_{zz}$ is the component more sensitive to the surface crystal field of the cationic site causing the $\Delta$ splitting. In the bottom of Fig. 4 a TEM picture of polycrystalline CaO materials. This solid
has been contacted with four different hydrocarbons (methane, ethane, propane and cicloexane) mixed with molecular oxygen. In all these cases no reaction is observed adsorbing the various mixtures on MgO whereas an appreciable amount of superoxide $\text{O}_2^-$ is produced by contact with CaO showing that at the surface of this oxide highly basic $\text{O}^{2-}$ sites are present capable of proton abstraction from these extremely stable molecules. Interestingly the spectral profile in the $g_{zz}$ region, magnified in the bottom of Fig. 4, differs in the four cases indicating that the sites where electron transfer occurs are not the same.

### 3.2.2 The $\text{O}^-$ Ion and the Homolytic Splitting of H–H and C–H Bond

While basic $\text{O}^{2-}$ ions are able, as shown before, of $\text{H}^+$ abstraction from $\text{R}–\text{H}$ (or H–H) bonds, the $\text{O}^-$ radical ions induce homolytic splitting of the same bonds with abstraction of H atoms.

The electron configuration of the $\text{O}^-$ ion is $[2p_x^2, 2p_y^2, 2p_z^1]$ and the corresponding $g$ tensor [43], in a simplified form and in the common case of an axial symmetry of the crystal field, can be written as

$$g_{zz} = g_{||} \approx g_e; \quad g_{xx} = g_{yy} = g_\perp = g_e + \frac{2\lambda}{\Delta E}$$

where $\lambda$ is the spin–orbit coupling constant for atomic oxygen and $\Delta E$ the energy splitting shown in Scheme 1.

The $\text{O}^-$ ion can be seen as an oxide ion trapping a hole. For this reason, this radical ion plays a fundamental role in photocatalysis processes. The initial step of a photocatalytic process is the light induced charge separation occurring in a semiconducting oxide (or in analogous systems) caused by photons. The absorption of photons with energy higher than the band gap causes the promotion of electrons from the valence band (VB) to the conduction band (CB) leaving behind a hole, according to the equation:

$$\text{MO} + \text{hv} \rightarrow h^+_{(\text{VB})} + e^-_{(\text{CB})}$$

After the excitation two opposite processes compete, that of charge recombination (detrimental for photocatalysis) and that of charge migration. In the case of semiconducting oxides used in photocatalysis when the photoexcitation experiment is carried out under vacuum a fraction of the photogenerated carriers can be observed by EPR either under continuous irradiation or after irradiation provided that the temperature is kept low enough to prevent recombination. An example is shown in Fig. 5 in the case of titanium dioxide. This oxide had the prominent role in the development of photocatalytic studies and it is still a benchmark in catalytic research. In the case of Fig. 5 the experiment concerns anatase, one of the three main polymorph of this oxide. The solid in the dark shows a nearly flat base line (Fig. 5a). The positive holes tend to localize on the oxygen ions ($\text{O}^{2-}$) of the lattice forming a paramagnetic $\text{O}^-$ ion

$$\text{O}^{2-} + h^+ \rightarrow \text{O}^-$$

whose typical signal is observed at $g > g_e$, (low magnetic field in Fig. 5b) according to Eq. 8. The photogenerated electrons are trapped on a metal cation sites producing trivalent

**Scheme 1** Energy levels of the $\text{O}^-$ radical ion (in axial symmetry)

**Fig. 5** Effect of UV irradiation on TiO$_2$ anatase. a EPR spectrum in the dark; b irradiation under vacuum; c irradiation under hydrogen atmosphere
titanium ions whose axial EPR signal \([44]\) is observed at higher magnetic field in Fig. 5b.

\[
\text{Ti}^{4+} + e^{-} \rightarrow \text{Ti}^{3+} \quad (11)
\]

The reactivity of the trapped hole \((\text{O}^{-} \text{ ions})\) and the ability in homolytic bond cleavage is shown performing the same type of irradiation under a hydrogen atmosphere. In this case the photoformed holes moving in the crystal reach the surface entailing the following series of reactions based on the ability of the surface hole centre \((\text{O}^{-})\) to cause the homolytic splitting of \(\text{H}_2\) generating reactive hydrogen atoms \([45]\)

\[
h^+_{(\text{VB})} + \text{O}^{-}_{(\text{surf})} \rightarrow \text{O}^{-}_{(\text{surf})} \quad (12)
\]

\[
\text{O}^{-}_{(\text{surf})} + \text{H}_2(\text{gas}) \rightarrow \text{OH}^{-}_{(\text{surf})} + \text{H} \quad (13)
\]

The highly reducing \(\text{H}\) atoms ionize at the surface transferring their electron to cationic centres of the solid, \(\text{Ti}^{4+}\) ions, whose reduction is monitored by EPR (Fig. 5c).

\[
\text{H}^+ + \text{O}^{-}_{(\text{surf})} + \text{Ti}^{4+} \rightarrow \text{OH}^{-}_{(\text{surf})} + \text{Ti}^{3+} \quad (14)
\]

The EPR signal of \(\text{Ti}^{3+}\) in Fig. 5c is therefore due to the combined effect of both photogenerated electrons, that are directly trapped by \(\text{Ti}^{4+}\) ions (Eq. 11), and photogenerated holes that operate through the mechanism described in Eqs. 12–14.

The reported example illustrates the particular role played by EPR in the investigation of photocatalytic processes. Since these are based on an initial event of charge separation and on a series of sequential charge transfer reactions, paramagnetic species are generated in all steps making photocatalytic phenomena an excellent playground for the applications of EPR.

Another important example involving surface \(\text{O}^{-}\) centres, that sparked a lot of interest in the catalytic community in the past, is the oxidative coupling of methane first reported by J. Lunsford and co-workers using a lithium promoted MgO catalyst (Li-MgO) and based, according to the Authors, on the reactivity of surface \(\text{Li}^+\text{O}^{-}\) centers \([46]\). The presence of \(\text{O}^{-}\) in this solid is ascribed to the valence induction caused by the insertion of the aliovalent \(\text{Li}^+\) in the MgO matrix. The stoichiometry of this system can, in principle, be written as \(\text{Li}^{+}_x\text{Mg}^{2+}_{1-x} \text{O}^{2-}_x \text{O}^{-}_x\). Surface exposed \(\text{Li}^+\text{O}^{-}\) centres in this material have been indicated, on the basis of EPR results, as responsible for the C–H cleavage \([47]\) according to

\[
\text{CH}_4(\text{g}) + \text{O}^{-}_{(\text{surf})} \rightarrow \cdot\text{CH}_3(\text{g}) + \text{OH}^{-} \quad (15)
\]

The \(\text{Li}^+\text{O}^{-}\) center are however rather elusive and the authors claim they exist in equilibrium state only at high temperature in the presence of oxygen. The resultant methyl radicals have been isolated using a matrix isolation technique at low temperature \([48]\). In catalytic conditions methyl radicals are either released in the gas to form ethane by radical coupling or trapped at the surface as methoxy species

\[
\cdot\text{CH}_3 + \text{O}^{2-} + \text{O}_2 \rightarrow \text{CH}_2\text{O}^{-} + \text{O}_2^{-} \quad (16)
\]

that entail a complex series of reactions, whose main products are ethane and carbon oxides.

The same Li–MgO system was revisited some years later in a thorough study on both films and powdered samples \([49]\). The features of the system resulted much more complex than previously observed and the solubility of \(\text{Li}^+\) was found quite inhomogeneous with formation also of oxygen vacancies and segregation of \(\text{LiO}_x\) clusters. \(\text{Li}^+\text{O}^{-}\) centers, in particular, were not observed, in this case, by EPR.

To this end it has to be kept in mind that paramagnetic species are not necessarily EPR visible in all conditions. This concept is appropriately illustrated by the example concerning Na doped CaO, a system analogous to Li-MgO, consisting in a monovalent dopant incorporated in a alkali-earth oxide matrix \([50]\). Na-CaO was prepared decomposing a sample of calcium carbonate containing

\[
\text{CH}_4(\text{g}) + \text{O}^{-}_{(\text{surf})} \rightarrow \cdot\text{CH}_3(\text{g}) + \text{OH}^{-}
\]

\[
\cdot\text{CH}_3 + \text{O}^{2-} + \text{O}_2 \rightarrow \text{CH}_2\text{O}^{-} + \text{O}_2^{-}
\]
sodium impurities and, after decomposition, it shows an EPR spectrum with a flat base line except for the presence of a weak sextet of hyperfine lines due to traces of Mn$^{2+}$, unavoidably occurring in calcium oxide (Fig. 6a). In Na-CaO the aliovalent Na$^+$ ions are actually compensated by O$^-$ centres that are not, however, EPR-active ($\text{Na}_x\text{Ca}^{2+}_{1-x} \text{O}^2_2 \text{O}^{2-}_{1-x}$O$^{2-}$) as they do not appear in the EPR spectrum of Fig. 6a. Their presence is however revealed by adsorption of molecular oxygen at low temperature. In such conditions the intense signal shown in Fig. 6b shows up which is due to the formation of ozone $\text{O}_3^-$ ions [51], whose $g$ tensor elements are well known. The ozonide species is formed according to a simple addition of molecular oxygen and requires the presence of O$^-$ at the surface:

$$\text{O}^-_{\text{surf}} + \text{O}_2(\text{gas}) \rightleftharpoons \text{O}_3^-_{\text{ads}}$$

(17)

It is worth mentioning that the same reaction is not observed in the case of undoped CaO and MgO that do not react with molecular oxygen. The ozonide adduct is unstable and decomposes rising the temperature. Remarkably, by a careful control of the experimental conditions (gentle vacuum annealing at 323 K and immediate quenching at 77 K) it has been possible to monitor an intermediate step of $\text{O}_3^-$ decomposition that leads to the formation of two new, partially overlapped, EPR signals. The former is due to a superoxide $\text{O}_2^-$ adsorbed on Ca$^{2+}$ (whose distinctive features is the $g_{zz}$ component at 2.10, (Fig. 6c) while the second is due to the perpendicular component of a O$^-$ signal having $g_\perp = 2.075$ as confirmed by a separate experiment of CaO irradiation by X ray with evidence of trapped electrons and trapped holes [50].

The O$^-$ species is observed in a restricted time interval since it progressively disappears upon prolonged annealing confirming its nature of elusive species. The decomposition mechanism of the ozonide ion is complex involving at least two distinct reaction channels. The whole stoichiometry is summarized by the following equation

$$3\text{O}_3^- \rightarrow 2\text{O}_2^- + \text{O}^- + 2\text{O}_2$$

(18)

The reason of the non-detectability of the O$^-$ radical ion in Na-CaO is not fully clear. It has to be recalled, however, that all experiments reporting a hole center in an oxide matrix concern cases of relatively low symmetry of the environment as it occurs in correspondence of a cation vacancy (the V centers [52] described in solid state physics) or at the surface of a solid. A tentative explanation considers that in case of a highly symmetric environment of the defect centre (small or nearly null $\Delta E$ value in Eq. 8) the resonance is expected to cover a wide range of magnetic field and its signal becomes practically undetectable. To conclude, the O$^-$ defect in Na-CaO is likely highly mobile and undetectable when moving in the volume of the crystal. The effect of oxygen adsorption is to trap the defect at the surface with formation of a rather labile ozonide ion stable in a limited range of temperature and oxygen pressure on the basis of the equilibrium reaction reported in Eq. 17.

### 3.3 Chemical Bonding at Solid Surfaces

#### 3.3.1 Probing the Nature of the Metal-Oxide Chemical Bond

When the interaction between an adsorbate and a surface site produces a paramagnetic entity, the EPR technique can be extremely powerful in describing in detail the features of the chemical bond occurring at the surface. We will discuss this point using two examples from the literature. The former concerns the bonding between single metal atoms and the surface of an oxide. It is well known in fact that, in principle, the catalytic properties of a given metal are conditioned by the interaction of the latter with the support (usually an oxide). By evaporation of alkali metals (Na, K, Rb, Cs) in contact with the surface of polycrystalline MeO (Me = Mg, Ca, Sr) the initial observed interaction leads to metal ionization and formation of surface trapped electron centers. However higher amounts of metal vapor produce paramagnetic centers characterized by a distinctive hyperfine structure typical of alkaline metals (all having non zero nuclear spin). We will discuss here in particular the case of potassium ($^{39}\text{K}, I = 3/2$, abundance = 93.6%).

The observed centers in this case contain a single metal atom since the signal consists in four lines arising from the hyperfine interaction of the unpaired electron with the nucleus of $^{39}\text{K}$, $I = 3/2$, and its structure is prevalently isotropic indicating the s character of the unpaired electron orbital (Fermi contact, see Sect. 2) with only some minor anisotropic contribution which causes a small distortion of the spectral structure.

The most relevant feature of this spectrum is the reduction of the hyperfine separation that drops out of about one half with respect to that of the free atom in the gas phase (4.14 mT vs. 8.23 mT) that is also reported in Fig. 7 (red trace). An initial hypothesis [53] of a partial delocalisation of the $4s^1$ electron spin density onto trapping sites of the solid surface was rejected by successive investigations employing MgO surface-enriched in $^{17}\text{O}$ [54] which is the only O isotope bearing a non zero nuclear spin ($I = 5/2$) and has been inserted on the surface by exchange with H$_2^{17}\text{O}$. The EPR spectrum of the monomeric center interacting with the isotopically enriched surface shows the onset of an additional sextet spaced by 0.28 mT on each K line proving that the metal atom is bound to surface oxygen ions with, however, a tiny degree of electron delocalisation towards the...
adsorbing site, not accounting for the observed lack of electron spin density with respect to the isolated atom. Further analysis by HYSCORE demonstrated that the single K atom interacts with at least three surface oxide anions. The model derived from this experimental finding involves a strong perturbation of the unpaired electron wave function caused by the polarizing interaction of the $O^{2-}$ lone pairs with the 4s orbital containing the K valence electron. This interaction destabilizes the latter orbital leading to an “expanded” atom structure reminiscent of a Rydberg state, with a sort of matrix-induced nephelauxetic effect. The Fermi contact term of the expanded 4s$^1$ orbital, whose energy is now mid-way between those of 4s and 5s orbitals of the unperturbed atom, dramatically decreases with respect to that of gas phase potassium without an effective electron delocalisation. This achievement could not have been fully acquired without the essential contribution of advanced theoretical calculations that corroborate this view and allowed the identification of a surface site involving three oxide ions with suitable geometry. This is the reverse corner site at the intersection with two perpendicular steps shown in Fig. 7. In this case the structure of the computed tensors confirms the drop of K hyperfine and the nature of the bonding. Furthermore, the calculated interaction energy (1.11 eV) is in line with the observed stability of the monomeric species up to room temperature. The molecular orbital scheme of the described surface interaction is illustrated in Fig. 8. The same type of phenomenon was observed in the case of K evaporation onto CaO and SrO. Interestingly, with increasing the basicity of the oxide (e.g. the donating ability of the $O^{2-}$ lone pairs) the polarizing effect increases and the $^{39}$K hyperfine constants further drop (Fig. 7) showing a linear correlation with the optical basicity of the three oxides [54].

The described bonding scheme is not limited to alkaline metals but it can be extended also to metals of higher interest for heterogeneous catalysis such as gold. The deposition of Au single atoms on the (001) surface of a MgO thin film enriched in $^{17}$O was investigated by Freund et al. [55] monitoring the interaction by the joint use of EPR and STM. Gold exhibits an electronic configuration analogous to that of alkaline metals ([Xe] 4f$^{14}$ 5d$^{10}$ 6s$^1$). A large reduction of the $^{197}$Au ($I = 3/2$) hyperfine coupling constant was observed upon deposition on MgO while the angular dependence of the $^{17}$O superhyperfine lines suggested the stabilisation.
of the metal atom on top of a single O$^{2-}$ ions of the (001) surface. Theoretical calculations confirm the idea that the large decrease of the isotropic hyperfine contact is not due to electron delocalisation but, rather, to a complex interplay between some degree of covalence (hybridisation of Au 6s and 5d with O 2p orbitals) and a pronounced polarisation of the 6s spin density, analogous to that described before for K on polycrystalline MgO [54]. Concerning the subject of metal atoms on solid surfaces it is worth mentioning that recently, electron magnetic resonance combined with scanning tunneling microscopy (STM) achieved single-spin sensitivity with sub-angstrom spatial resolution. EPR-STM has been successfully used for the study of magnetic properties and interactions of individual transition metal atoms (Ti, Fe) adsorbed on MgO [56–58].

A case somehow parallel to that described above was followed investigating the interaction of Zn and Cd monovalent ions (both paramagnetic having ns$^1$ configuration) with the framework of a ZSM-5 zeolite enriched with $^{17}$O via a series of hydration-dehydration cycles using water vapour enriched with H$_2$$^{17}$O [59]. These two metal ions have been recently considered as active centres in the activation of small hydrocarbon molecules [60, 61]. The interaction of Zn$^+$ and Cd$^+$ with the framework is investigated monitoring the $^{17}$O hyperfine by X-band CW-EPR and Q-band HYSCORE. Zn$^+$ coordinates to two equivalent oxygen atoms forming an adduct with pseudo C$_2$v symmetry while the equivalent Cd$^+$ is less symmetric with two non-equivalent framework oxygen. Coupling these results with DFT modelling it was possible to individuate the framework sites where the interaction occurs. The picture of the interaction between the two monovalent cations of Group XII and the zeolitic framework is different than in the previous case (K-MgO) since about 10% of the electron spin density originally present on the ns$^1$ systems is transferred onto the lattice oxygen to form a chemical bond with ionic-covalent character. As it will be illustrated in the following of the present paper, $^{17}$O labelling is becoming an extremely powerful tool to explore the chemical bonding in oxide-based catalytic systems.

### 3.3.2 Chemical Bonding in Surface Adducts of Transition Metal Ions

Isolated transition metal ions incorporated in the framework of zeolites have an utmost importance in modern catalysis. For example, 30 years after the first reports on nitric oxide decomposition on Cu$^{2+}$-exchanged zeolites [62, 63], this subject remains a highly current topic in research [64]. Central aspects of the catalytic chemistry of these materials are both the transformation of Cu$^{2+}$ sites in Cu$^+$ and the features of the chemical bond in the reaction intermediates between NO and the cuprous ions that are critical to explain...
the catalytic action [65]. As to the latter aspect, EPR have played in the past an important role due to its intrinsic ability to unravel details of the chemical bonding when paramagnetic species are involved. In particular, the nature of the interaction between Cu⁺ ions and NO in Cu-ZSM5, widely investigated in the past, is briefly mentioned here to illustrate the delicate balance between donation and back-donation operating in these transition metal adducts. When NO is contacted with a pre-reduced material mainly containing Cu⁺, an intense spectrum is observed by CW-EPR (Fig. 9) which is characterized by hyperfine interactions due to [63, 65] Cu nuclei, both having \( I = 3/2 \), and to \(^{14}\)N (\( I = 1 \)) [66].

Simulation and analysis of the spin-Hamiltonian parameters allowed to unravel the features of a Cu⁺NO species with η¹bent structure and characterized by monoclinic symmetry, e.g. the non-coincidence of the axes of \( g \) and \( A \) tensors. The main fraction of the electron spin density is localized on the coordinated NO molecule with, however, a relevant degree of delocalisation from the π antibonding NO orbital onto copper orbitals through the bond drafted in Fig. 9 [67]. This is based on the overlap of Cu⁺ 3d_{z^2}, 3d_{x^2} and a lone pair N orbital (n) with a NO 2π* which determines the SOMO, while the interaction of 3d_{xy} and the other NO 2π* originates the LUMO. The large value of the isotropic component of the hyperfine constant (Fermi contact) is due to both the spin polarisation of inner Cu s-orbitals and to a contribution of spin delocalisation onto the 4s one. The total spin densities are about 0.2 for copper, 0.55 for nitrogen. The remaining spin density (0.25), not accounted for by the EPR spectrum, is on oxygen. The described nitrosyl adduct is rather labile and can play a role in further NO reactivity. It has been hypothesized in fact that an electrophilic attack of a second molecule in the gas phase to the activated nitrosyl leads to the formation of a N–N bond, essential step for the direct decomposition of nitric oxide. Successive experimental work using multifrequency EPR and pulse EPR has further contributed to the characterisation of this important intermediate [68, 69] while advanced computational investigations have nicely confirmed and further detailed the picture of the chemical bond derived from EPR [70–72].

This bonding interaction is of relevance in the context of the abatement of NOx pollutant where nickel-exchanged zeolite catalysts have also received a considerable scientific interest due to their capability to promote the HC-SCR reaction with both unsaturated and saturated hydrocarbons, comprising methane [73]. In this context, the mechanistic aspects of model selective catalytic reduction (SCR) of NO with C₂H₄ over Ni/ZSM-5 zeolite were recently investigated by means of advanced correlation EPR/HYSCORE methods, revealing fine details of the electronic and magnetic structure of Ni²⁺–NO [74].

![Fig. 10 Top: CW-EPR spectrum of Ti³⁺ in hydrogen reduced Ti-AlPO and scheme of the catalytic site. Bottom: HYSCORE spectrum of Ti³⁺ in the AlPO framework](image)

### 3.4 Topological Description of Active Sites in Catalytic Systems

The potential of EPR techniques in the investigation of heterogeneous catalysts is primarily related to the observation of hyperfine and superhyperfine interactions with the surroundings. CW-EPR has an intrinsic limitation in this context since the interaction between electron and nuclear magnetic moments are usually resolved when they are large enough in comparison with the intrinsic linewidth of the signal. This implicates that superhyperfine interactions with the first coordination sphere of the paramagnetic centre, and a fortiori with the second sphere, are seldom detected by CW-EPR. The advent of pulsed methods in EPR has open new perspectives in this area since the magnitude of detectable hyperfine splitting is comparable to NMR resolution. To this end the two following examples are paradigmatic. Both concern subtle structural and topological aspects of two important catalytic systems whose features have been disclosed using pulsed EPR and, in particular, the so called hyperfine techniques.

#### 3.4.1 Open Framework Systems

Aluminophosphates molecular sieves (AlPOs) are a family of zeotype materials [75] that, more easily than aluminosilicates, can incorporate transition metal ions into their framework giving origin to new materials with high...
potential for applications in heterogeneous catalysis. The neutral network of AlPOs is made up by connected tetrahedral units of AlO4 and PO4. Particularly interesting is the case of the incorporation of Ti4+ ions that adds the redox properties typical of the transition ion to the acidic ones typical of the AlPO-4 network [76]. Several questions have been debated in the literature about this system, in particular concerning the site of isomorphous substitution (P or Al), the role of Ti ions in redox chemistry and their availability to coordinating molecules. EPR techniques have played a crucial role in this debate. The system is in fact reducible and by thermal treatment at 673 K in hydrogen atmosphere the EPR signal of a Ti3+ ions shows up as illustrated in Fig. 10. The reduction of Ti4+ is accompanied by stabilisation of an H+ by an oxygen of the network to maintain the electric neutrality.

\[
\text{Ti}^{4+} + \text{O}^{2-} + 1/2 \text{H}_2 \rightarrow \text{Ti}^{3+} + \text{OH}^- \quad (19)
\]

Due to the low abundance of isotopes with I ≠ 0 no Ti hyperfine is usually observed in Ti3+ powder spectra and the information is limited to the g tensor. However the dependence of the g tensor on the symmetry of the environment is well known [18, 19, 77] and the nearly axial signal in Fig. 10 is unambiguously associated to ions in the tetrahedral crystal field of four oxygen atoms thus showing that titanium ions are indeed incorporated in the AlPO framework. The specific location of the reduced ion however does not show up from the CW spectrum. The two possible situations imply a difference in the second coordination sphere that is composed by Al ions in the case of isomorphous substitution at the P site and vice versa. Both 27Al (I = 5/2) and 31P (I = 1/2) have 100% natural abundance but the tiny superhyperfine interaction with the unpaired electron on Ti3+ is not perceptible in natural abundance but the tiny superhyperfine interaction using HYSCORE. The spectrum reported in the bottom of Fig. 10 shows the cross peaks ascribable to the interaction of the unpaired electron with four distinct 31P nuclei [78]. The only trace due to 27Al is due to remote nuclei.

This experiment therefore demonstrates that titanium ions are actually inserted in the tetrahedral framework and, additionally, that the reducible titanium ions are those replacing Al in the AlPO network (Scheme in Fig. 10, top). The 31P coupling constants measured in the HYSCORE experiment range from 10 to 30 MHz and, as expected, are too small to be directly observed by CW-EPR. The tetrahedral Ti3+ ions are coordinately unsaturated and their coordination sphere is modified by adsorption of Lewis bases such as water and ammonia. In this latter case two NH3 ligands bind to the catalytic centre whose hyperfine and quadrupole 14N coupling tensors have been fully resolved [79]. The same approach here illustrated was also followed for the characterisation of vanadium centres in the framework of monometallic VAiPO-5 [80] and bimetallic VTiAlPO-5 catalysts with relevant catalytic activity and selectivity in aerobic oxidations [81]. In this case, HYSCORE and EPR were key to demonstrate that well-defined and isolated oxophilic tetrahedral titanium centers coupled with redox-active VO2+ ions at proximal framework positions provide the loci for the activation of oxidant that boosts the catalytic activity compared to analogous monometallic systems.

### 3.4.2 Ziegler–Natta Catalysts

Ziegler–Natta (Z–N) systems for the production of polyolefins are highly effective catalysts that, in spite of a great deal of investigations and of about 60 years of industrial application, remain rather elusive. ZN catalysts are very complex systems whose main components are titanium ionic species generated adsorbing a precursor (most often TiCl4) on the surface of magnesium dichloride. The catalyst however needs of a cocatalyst (usually an aluminium alkyl) that reduces the adsorbed Ti species producing in this way the active sites for the polymerisation reaction. EMR techniques, coupled with DFT calculations, have contributed to shed some light on the nature of surface reduced Ti species present at the surface of an activated Z–N catalyst.

An early report by Schmidt et al. [82] has been, at the same time, the first EPR study of the surface of a single crystal and the first surface science investigation of a Ziegler–Natta catalyst. A (001) crystal face of MgCl2 was prepared by evaporation employing a Knudsen cell. TiCl4 could be adsorbed on this surface only after increasing the defect density by ion bombardment and reduced Ti3+ centers were so observed by EPR. The system however becomes catalytically active only after interaction with aluminium alkyl ad shown by the direct EPR detection of ethyl radical by EPR.

X-band continuous wave (CW) EPR techniques have been largely used in the characterization of real ZN catalysts primarily to monitor and quantify the amount of reduced Ti species [83–85]. In the case of supported titanium–magnesium catalysts with a low titanium content (≤ 0.1wt%), isolated mononuclear Ti(III) species have been reported to form on the surface at a high yield (40–70% of the total titanium content). Moreover, a correlation was found between the content of the isolated Ti(III) species and the activity of these catalysts in ethylene polymerization [86]. The observed g values for activated ZN catalysts depends on many factors, including the presence of coordinated AlR3 co-catalysts, the potential coordination of Lewis basis and the localization at different surface terminations of the MgCl2 support. Tregubov et al. [87] reported spectra with two Ti(III) signals.
with axial $g$ tensor ($g_{∥} = 1.984$, $g_{⊥} = 1.966$ and $g_{∥}^{1,2} = 1.79$) for a supported TiCl$_4$/MgCl$_2$ system obtained by the reduction with triisobutylaluminium (TIBA). EPR spectra of the TiCl$_3$-0.3AlCl$_3$ catalyst showed a signal with $g_{⊥} = 1.94$ and $g_{∥} = 1.90$ (with a concentration of just 1% of the total titanium content) [88].

More recently CW and pulse-EPR were applied to investigate the surface of a fourth generation Z–N catalyst. A MgCl$_2$/TiCl$_4$/dibutylphthalate precatalyst (2% Ti by weight) was treated in situ with triethylaluminium (TEA) vapors and investigated by EMR following a multifrequency approach [89]. The intense EPR spectrum, due to Ti$^{3+}$ centers, observed upon this treatment concerns some 15% of the total titanium content. Despite the complexity of the catalytic system the EPR spectrum is well defined and can be interpreted, according to the computer simulation, as the overlap of two main Ti$^{3+}$ signals (Fig. 11a) corresponding to two distinct surface sites. HYSCORE experiments show that Ti$^{3+}$ centres are coordinated to Cl atoms as shown by the ridges in Fig. 11a’ related to the interaction with $^{35}$Cl and $^{37}$Cl both having $I = 3/2$. TiCl$_3$ molecular complexes are therefore formed, compatible with the location on MgCl$_2$ (110) faces as indicated by DFT modelling. The accessibility of such sites (an important parameter to unravel the nature of catalytically active sites) was tested by adsorption of oxygen with consequent electron transfer and formation of superoxide O$_2$•− radical ions stabilized on top of Ti$^{4+}$ (Fig. 11b) whose signal is well known. Oxygen reacts with about 60% of the Ti$^{3+}$ ions generated at the surface. The remaining centers are therefore not exposed at the surface. The EPR analysis of the Ti$^{3+}$ centers however, does not provide any information about the TEA co-catalyst although this contains Al nuclei with non-zero nuclear spin. To this end, the O$_2$•− centres constitutes a second paramagnetic probe to be exploited for a further monitoring of the environment. Remarkably Q-band HYSCORE shows two $^{27}$Al cross peaks (Fig. 11b’) indicating a direct interaction of this radical with an Al ion. The above results as a whole, resumed by the pictorial scheme in the Figure, represent an important step in the search of a satisfactory description of a highly important however elusive catalytic system. Following this first report, the use of advanced EPR techniques in this field has been successfully applied to investigate molecular complexes and surface species for olefines polymerization [90–93].

![Fig. 11](https://example.com/fig11.jpg)

Fig. 11 Top: X-band CW-EPR spectra of the activated Z–N catalyst before (a) and after (b) contact with O$_2$. Bottom: HYSCORE spectra showing the hyperfine interaction of Ti$^{3+}$ with Cl (a’) and that of O$^{2−}$ with Al. The scheme report the structure of the whole centre as derived by EMR.
3.5 Geometrical and Electronic Structure of Catalytic Sites Via Selective Isotopic Enrichment

An obvious mandatory conditions for the observation of hyperfine structures in a EPR spectrum is the presence of “magnetic” nuclei (I ≠ 0) in the chemical environment of the paramagnetic centre. The isotopic composition of oxygen in natural abundance is dominated by nuclei with I = 0 (16O, 99.76% and 18O, 0.2%) while 17O, with I = 5/2, represents a fraction of about 0.04% only, with absolutely no chance to produce a detectable hyperfine structure in EPR spectra. This fact constitutes a severe limitation in catalytic studies considering the dominant role of oxygen in the composition of heterogeneous catalytic systems. Initially, and for several years, the 17O isotopic labelling was limited to the use of enriched gaseous oxygen [38] to characterize the structural features of surface adsorbed species. Only more recently our group started a more systematic effort of incorporating the isotope at the surface [94] or in the bulk [95] of the investigated oxide materials as it has been also shown, for instance, in the examples reported in Sect. 3.3.

The joint use of 17O isotopic labelling and pulse-EPR technique (that extend the monitoring to weak electron–nuclear interaction viz. to atoms more distant from the paramagnetic centre) represents a tremendous improvement of quality in catalytic research by EMR methods. The following example, concerning a system obtained by evaporation of VCl4 onto the framework of a H-ZSM-5 zeolite [96], illustrates the potential of this approach in terms of structural characterisation of a catalytic site.

CW-EPR spectra (Fig. 12 top) suggest the presence of isolated vanadylic VO2+ species formed upon dechlorination of the precursor and provide the measure of the 51V hyperfine structure. Q-band HYSCORE experiments allow to measure the weaker hyperfine interactions with both 27Al (Fig. 12 bottom, revealing the nature of the zeolite framework site of V grafting) and 1H (unravelling the presence of a hydroxyl group in the coordination sphere of the metal).

The atomistic description of the catalytic site, however, is exhaustive only including the information about the framework oxygen in direct interaction with the vanadium centre. This was achieved introducing 17O in the zeolite by preliminary cycles of hydration–dehydration performed using 17O enriched water.

17O incorporation selectively occurs at the active sites and allows the measure of well resolved 17O HYSCORE spectra once that the reaction with VCl4 has been performed. In this case, the HYSCORE spectra (Fig. 12 bottom) clearly show the interaction of the nuclei with the framework oxygen and the vanadium centre. The analysis of these spectra provides important information about the local environment of the vanadium centre, including the nature of the coordination sphere and the orientation of the dipole moments of the nuclei.

Fig. 12  Top: X-band (left) and Q-band (right) CW-EPR spectra of the vanadylic centres in 17O enriched ZSM-5 zeolites prepared by evaporation of VCl4. Bottom: HYSCORE spectra monitoring 27Al (left) and 17O hyperfine interaction and structural scheme of the catalytic centre.
way the full set of hyperfine constants related to the first
and second coordination sphere of Vanadium are obtained
allowing to derive a thorough structural model of the centre
(bond lengths and bond angles, Fig. 12) rivalling in terms
of details with those derived from X-ray techniques. This
element definitely shows the enormous potential, in terms
of structural description, resulting from coupling the whole
arsenal of CW and pulse EPR techniques with a selective
isotopic enrichment of the solid.

4 Conclusive Remarks

In the present manuscript some of the main aspects of surface
chemistry and heterogeneous catalysis that can be conveni-
ently addressed by EMR techniques have been illustrated. We
have tried to emphasize, on the one hand, the ability of these
techniques in monitoring reaction intermediates that are often
labile and low-concentration entities. On the other hand, we
have outlined their strength in the structural and electronic
characterization of chemical systems at the surface of solids
(mainly oxides, zeolites and other porous systems) that is
essentially based on the ability to monitor the interactions of
the unpaired electron with its atomic environment. However,
trying to answer the second question posed in the introduction
about the convenience of introducing EPR instrumentations in
the arsenal of a modern laboratory of surface chemistry and
catalysis, it appears that these are not simply “plug and play”
machines, easily exploitable without a deep specific scientific
background. To obtain results going beyond simple analytical
data (is a given paramagnetic species present in a system?) it
is necessary to handle the complex physics of magnetic inter-
actions. Moreover, pulse-EPR experiments are complex and
must be carefully designed in advance to obtain significant
results whose interpretation is delicate and non-straightfor-
ward. Therefore, since EPR instrumentations, and in particular
advanced ones, are rather expensive, it can be inconvenient to
invest important resources in an EPR tool without the training
necessary to exploit its potential to the maximum level.

Working instead with an adequate background, there are
clear advantages in having an EPR instrumentation available
in an advanced laboratory of surface chemistry and catalytic
sciences. In particular, the ability to measure the electron spin
density in the catalytic site and in its surroundings, hence
obtaining detailed information on the nature of the SOMO,
is a resource of invaluable importance that goes directly to
the heart of the chemical interaction as in a few other cases
only. To this important point we must add another aspect that
only partially emerges from the examples illustrated above.
It is the coupling between experimental results and advanced
computational methods that is particularly fruitful in the case
of EMR techniques. Modern DFT methods are now able to
produce highly accurate results in the calculation of EPR and
NMR magnetic tensors [97] and several quantum chemical
packages have made such calculations relatively accessible.
The computational approach becomes therefore a further tool
that supports the various CW and pulsed techniques and, in
particular, it results highly useful when the EPR data alone are
not sufficient to select the correct solution among two or more
structural hypotheses compatible with the experimental data.

In conclusion, EMR techniques have, like all experi-
mental techniques used in the world of solid surfaces and
catalytic sciences, strengths and weaknesses. We have tried
to demonstrate in this paper that the strengths are so impor-
tant, at the present stage of technological developments of
the hardware, that a future season of wider use of Electron
Magnetic Resonance in these scientific areas can be confi-
dently foreseen.

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