Single Metal Atoms on Oxide Surfaces: Assessing the Chemical Bond through $^{17}$O Electron Paramagnetic Resonance

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CONSPICUS: Even in the gas phase single atoms possess catalytic properties, which can be crucially enhanced and modulated by the chemical interaction with a solid support. This effect, known as electronic metal−support interaction, encompasses charge transfer, orbital overlap, coordination structure, etc., in other words, all the crucial features of the chemical bond. These very features are the object of this Account, with specific reference to open-shell (paramagnetic) single metal atoms or ions on oxide supports. Such atomically dispersed species are part of the emerging class of heterogeneous catalysts known as single-atom catalysts (SACs). In these materials, atomic dispersion ensures maximum atom utilization and uniform active sites, whereby the nature of the chemical interaction between the metal and the oxide surface modulates the catalytic activity of the metal active site by tuning the energy of the frontier orbitals. A comprehensive set of examples includes fourth period metal atoms and ions in zeolites on insulating (e.g., MgO) or reducible (e.g., TiO$_2$) oxides and are among the most relevant catalysts for a wealth of key processes of industrial and environmental relevance, from the abatement of NO$_x$ to the selective oxidation of hydrocarbons and the conversion of methane to methanol.

There exist several spectroscopic techniques able to inform on the geometric and electronic structure of isolated single metal ion sites, but either they yield information averaged over the bulk or they lack description of the intimate features of chemical bonding, which include covalency, ionicity, electron and spin delocalization. All of these can be recovered at once by measuring the magnetic interactions between open-shell metals and the surrounding nuclei with Electron Paramagnetic Resonance (EPR) spectroscopy. In the case of oxides, this entails the synthesis of $^{17}$O isotopically enriched materials. We have established $^{17}$O EPR as a unique source of information about the local binding environment around oxygen of magnetic atoms or ions on different chemical properties (i.e., basicity or reducibility). Emphasis is placed on chemical insight at the atomic-scale level achieved by $^{17}$O EPR, which is a crucial step in understanding the structure−property relationships of single metal atom catalysts and in enabling efficient design of future materials for a range of end uses.

KEY REFERENCES

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1. INTRODUCTION

“Adsorbed, chemisorbed, embedded, anchored, grafted” are all different words used to describe the variety of bonding between an atom and the surface of a support. Spatially isolated metal atoms on surfaces represent a relevant class of heterogeneous catalysts, referred to as “single atom catalysts” (SACs). Here “single atom” denotes well isolated and atomically dispersed species at specific surface sites. The basic rules of chemistry apply to this interfacial situation, which define the interaction between the atom and the surface as dispersive, covalent or ionic depending on the degree of orbital overlap and energy difference of the interacting orbitals. The understanding of such interactions grew up in parallel with the development of methods for the controlled deposition of metal particles and, in general, with the improvement of the performances of advanced surface science and computational techniques. Evolving from early models, the evidence of an enhancement of the catalytic activity induced by electronic metal−oxide interactions grew up in parallel with the development of methods for the controlled deposition of metal particles and, in general, with the improvement of the performances of advanced surface science and computational techniques. The recent combination of EPR with scanning tunneling microscopy (STM) enabled addressing the EPR signature of an individual atom on the surface. In the case of metals on oxide surfaces, the coupling between the electron and nuclear spins is a unique source of information about the local binding environment around the open-shell metal center that allows one to rationalize structure−property relationships in the most diverse systems. In our laboratory, EPR has been used over the past 15 years to investigate the interaction of single paramagnetic metal atoms or ions with different oxidic supports in order to monitor the redistribution of the electron spin density and to understand, in this way, the specific features of the metal−oxide chemical interaction. Here we will focus on single atoms and ions with complementary valence electron configurations across the fourth period of the periodic table, from K to Zn, and their interactions with oxide substrates featuring complementary chemical properties (Figure 1).

2. 17O HYPERFINE SPECTROSCOPY

Single metal species interact with oxide surfaces forming new bonds at the interface, which can range from weak interactions, dominated by dispersive forces and polarization effects, to covalent bonds, involving the mixing of metal and oxide orbitals, up to net electron transfer interactions resulting in ionic bonds. All these situations, which crucially depend on the nature of the oxide support, can be monitored with EPR spectroscopy. For open-shell metals, the spin, and its delocalization, is central in dictating design principles for the development of new sustainable catalytic pathways and plays a key role in the evolution of new materials and quantum information technologies.

A powerful yet underexploited experimental technique is Electron Paramagnetic Resonance (EPR) because of its intrinsic ability to monitor the electron spin density in paramagnetic systems. EPR has been successfully applied to study ensembles of single atoms dispersed on polycrystalline surfaces—the object of this Account—and on thin oxide films. Noteworthy, the recent combination of EPR with scanning tunneling microscopy (STM) enabled addressing the EPR signature of an individual atom on the surface. 

Figure 1. Single metal atoms and relative oxide supports described in this Account. For each element, including oxygen, the relevant magnetic properties are listed: isotope (\(A\)), nuclear spin (\(I\)), nuclear g factor (\(g_n\)), and natural abundance (\%Ab).
The hyperfine interaction splits the EPR resonance transition in \(2nI + 1\) hyperfine lines, where \(n\) is the number of equivalent nuclei and \(I\) is the nuclear spin quantum number. Therefore, the number of hyperfine lines in the EPR spectrum directly identifies the presence of a single metal species (\(n = 1\)) through the detection of \(2I + 1\) transitions. The integrated intensity of a Continuous Wave (CW) EPR spectrum is directly proportional to the concentration of spin species (free electron, \(g_e = 2.0023\)) on a \(^{17}\)O nucleus with a uniaxial spin population (\(I_s = 1\)) in an s-type orbital, one would observe an isotropic hyperfine coupling constant of \(a_s = -4622.83\) MHz. If the electron resides in a p-type orbital, one would observe a uniaxial hyperfine constant of \(b_p = 130.5\) MHz. Including a correction for the difference in the \(g\) values, the spin populations in s-type and p-type orbitals can thus be estimated as

\[
\rho_s = \frac{a_{iso}}{a_0} \frac{g_e}{g_{iso}}; \quad \rho_p = \frac{T}{b_0} \frac{g_e}{g_{iso}}
\]

For instance, for the case relevant to this Account—a single metal atom on an oxide surface—the ratio of the measured isotropic and dipolar hfc to the corresponding values for the free atomic state quantifies the contribution of the metal atomic orbitals to the molecular orbital containing the unpaired electron. On the other hand, the hfc with \(^{17}\)O nuclei reflects the electron spin density distribution over the coordinating ligands, which provide a clear-cut answer to the thorny question on how metals bind on oxide surfaces.

Experimentally, hfc can be directly detected in a standard CW-EPR experiment if large enough. If small, they can be recovered by means of hyperfine techniques such as Electron Nuclear Double Resonance (ENDOR), Electron Spin Echo Envelope Modulation (ESEEM) and Hyperfine Sublevel Correlation (HYSCORE) spectroscopies, which exploit the interaction between electron and nuclear magnetic moments to measure the NMR spectrum associated with the paramagnetic center. ENDOR experiments (in both CW or pulse variants) are based on a combination of micro- and radiowaves to measure the response of the electron spin as an incident radio frequency (rf) sweeps through different nuclear

\[
a_{iso} = \frac{2\mu_0}{3} \frac{\mu_B g_s}{\mu_N g_N} \rho_s^{g-s} \rho_s^{g-p}
\]
transitions. ESEEM and HYSCORE are based on a sequence of microwave (mw) pulses to generate an electron spin echo, whose intensity is monitored as a function of the variation of one or more time intervals between the pulses. The resulting time-domain signal is modulated by the nuclear frequencies, and after Fourier transformation a frequency-domain spectrum reproducing the nuclear frequencies is obtained.

In general, the two classes of hyperfine techniques give complementary information. ESEEM techniques are mainly used to detect small hfc (<5 MHz), while ENDOR techniques are usually preferred to observe larger nuclear frequencies, i.e., larger hfc.

3. \textsuperscript{17}O SURFACE DOPING OF METAL OXIDES

Hyperfine techniques require the presence of magnetic nuclei (i.e., nuclei having a spin). In the case of oxides this implies magnetic oxygen ions. Oxygen has only one magnetic isotope, \textsuperscript{17}O, characterized by a high spin quantum number \(I = 5/2\) and a natural abundance (0.038%), far too low to detect any hyperfine structure in naturally occurring samples. The exploitation of hyperfine techniques to assess the metal–oxygen bond requires therefore isotopic enrichment of the oxide matrix. This involves cost and effort but can be very rewarding. In the case of polycrystalline materials, the high cost of \textsuperscript{17}O isotopically enriched reagents makes bulk synthesis very inconvenient. Moreover, opposite to \textsuperscript{17}O NMR studies, where uniform substitution of \textsuperscript{17}O throughout the lattice is often sought to allow for quantitative measurements, selective isotopic enrichment can be advantageous in the case of EPR studies of single atoms on the surface. \textsuperscript{17}O surface enrichment can be performed following specific procedures that depend on the nature of the oxide. For nonreducible oxides (such as alkali-earth metal oxides, alumina, zeolites, etc.) the preferred isotope carrier is isotopically labeled water (\(\text{H}_\text{2}\text{}{\textsuperscript{17}}\text{O}\)). In this case hydration/dehydration cycles using \(\text{H}_\text{2}\text{}{\textsuperscript{17}}\text{O}\) vapors provide an effective and atom-efficient method to incorporate \textsuperscript{17}O isotopes at the surface. By adjustment of contact time and temperature, the process can be selective, limiting the isotopic exchange to the most reactive surface sites, which are the very sites involved in the stabilization of surface single atoms.

In the case of rock-salt structures such as MgO (Figure 2a), the exchangeable and chemically relevant sites correspond to three- and four-coordinated oxygen ions at corners and edges, whereas five-coordinated sites at dominant (100) faces are less involved in the exchange process. Similarly, zeolite (Figure 2b) can readily exchange their Si–O–Al and Si–O–Si framework sites with the oxygen of \(\text{H}_\text{2}\text{}{\textsuperscript{17}}\text{O}\), while keeping their highly crystalline frameworks. The reactivity order is Si–O–Al > Si–O–Si, where Si–O–Al are the privileged metal binding sites because of charge compensation. The reported isotopic enrichment protocols were carefully scrutinized against structural or morphological alteration of the pristine oxide materials. Such careful structural characterization should always be performed when water is employed as isotopic carrier in light of possible oxide sintering or Al leaching from the zeolite framework.

For reducible oxides such as TiO\(_2\) (Figure 2c), the strategy exploits the easy lattice oxygen depletion at the surface achieved by thermal treatments under vacuum. This generates oxygen vacancies, which can be replenished by heating in \(\text{O}_2\) atmosphere. Due to the surface nature of oxygen vacancies,
this method ensures a selective isotopic enrichment of the surface.51

4. THE EFFECT OF ACID–BASE PROPERTIES OF THE SUPPORT: SINGLE METAL ATOMS AND IONS WITH 4s1 ELECTRON CONFIGURATION

Central to the problem of the metal atom–oxide interaction is the ability to monitor the electron spin density distribution over the atoms of the support. While the number of EPR lines and their relative intensity provides direct compelling evidence for the presence of single metal atoms on the surface, the hfcs with ligated atoms of the support encodes important information on the electronic structure and binding geometry. A paradigmatic example is that of neutral alkali metal atoms stabilized on the surface of alkaline earth oxides,17,20,52,53 which represent an excellent test-bed to interpret the bonding mechanisms of neutral metals on nonreducible oxides.20 In the following we will discuss the case of K on MgO (K/MgO, Figure 3a).

The four hyperfine lines observed in a standard CW-EPR spectrum (Figure 3b) are due to the interaction of the unpaired electron with the 1 = 3/2 nuclear spin of K and firmly demonstrate the presence of single potassium atoms on the surface of MgO.1 The EPR spectrum of Figure 3b proves that surface K species retain the recognizable parentage of alkali metal atoms in the gas phase, but are subject to large perturbations arising from strong atom–surface interactions. In fact, the isotropic hfcs of the metal is reduced by about 50% as compared to that of gas phase K atoms.54 A naive interpretation may point to a partial charge transfer from the metal to the surface. However, analysis of the complementary 17O hfc in an enriched Mg17O sample showed that K atoms bind strongly to two surface oxygen ions (O1 and O2 in Figure 3a) and weakly to a third (O3 in Figure 3a), but the measured maximum 17O hfc of ≈9 MHz is far too small to account for a significant spin delocalization over the matrix ions.1 This evidence thus firmly excludes that the origin of the lowered hfc observed at the K nucleus is due to a spin (charge) delocalization over the oxide support. In fact, the mechanism responsible for the reduction of the spin density at the K nucleus1 is principally a polarization of the singly occupied 4s orbital of neutral K atoms induced by Pauli repulsion effects brought about by the lone pairs of surface oxygens. The net result of this interaction is to lift in energy the 4s K orbital, favoring some degree of sp hybridization. This “expanded atom” (or polarized) state explains the reduced hfc with respect to the free atom without invoking any significant metal to surface electron transfer. This is a general bonding scheme for neutral metals on the surface of basic oxides20 and depends on the degree of interaction between the oxide ion lone pairs and the ns orbital or, in other words, on the basicity of the oxide. A systematic study of alkaline earth oxides demonstrated that the reduction of the metal hfc linearly correlates with the well-known trend of basic strength MgO < CaO < SrO < BaO.55

To fully appreciate the role of the substrate, it is instructive to compare the data on MgO to a different oxide substrate featuring opposite characteristics, i.e., a covalent and acidic nature, namely, zeolite (Figure 3d). Zeolites are composed of corner sharing SiO4 and AlO4 tetrahedra, arranged into three-dimensional frameworks in such a manner that they contain regular channels and cavities of molecular dimensions. The substitution of aluminum (formally Al3+), in place of silicon (Si4+), produces a net negative charge, which is balanced by acidic (Bronsted) protons (or other cations) resident in the cavities. When incursive atoms from the vapor of, for example, alkali metals enter a dehydrated zeolite, they are spontaneously ionized reducing the acidic protons and forming a variety of unusual ions, clusters, and filamentary structures.55 Particularly interesting to our discussion is the case of zinc. The exposure of a protonated zeolite to Zn vapors leads to the reduction of H+ Bronsted sites and the formation of the unusual monovalent Zn+ species, characterized by a 4s0 electronic structure, which are iso-electronic with K.56 The EPR spectrum of sublimated Zn in zeolites is characterized by a nearly isotropic signal flanked by six evenly spaced satellite transitions due to the hfc with 65Zn (I = 5/2, 4.1% natural abundance).

While the six satellite transitions (Figure 3e) provide evidence for the presence of single metal ions, analysis of the 65Zn hfc points to 80% electron spin density localization in the 4s Zn orbital, proving the formation of a genuine Zn+ ion. The 20% missing spin density is shared between two equivalent coordinating oxygen atoms as testified by the 11 hyperfine lines (hfc ≈ 60 MHz) of the 17O EPR spectrum (Figure 3f). While the local metal coordination is similar for K/MgO and Zn/ZSM-5, the electronic structure is dramatically different. The coordinating oxygen ions of the ionic and basic MgO strongly polarize the K atom wave function with a minute spin delocalization to the surface (17O hfc ≈ 9 MHz); on the other hand the more covalent and acidic zeolite yields a bond mostly ionic, with a non-negligible degree of covalency (17O hfc ≈ 60 MHz). This comparison illustrates the unique level of details provided by 17O hfc in the description of the metal coordination environment in disordered systems.

This knowledge allows us to pinpoint the structure of the metal binding sites with atomistic precision and discriminate among different potential binding sites and it is the prerequisite to map the spatial distribution of single metal atoms in the nanometer range.57 When the 17O hfc is large enough to be resolved, the CW-EPR spectrum provides a handle to assess the level of isotopic enrichment at the metal site. In the case of K/MgO and Zn/ZSM-5, both characterized by a digonal coordination, this is done by comparing the relative intensity of the 17O hfc pattern and assuming a binomial distribution. In this way, we estimated a 10% 17O enrichment for K/MgO1 and a 70% enrichment for Zn/ZSM-5.5 Considering the procedure described in section 3, we note that the isotopic enrichment is metal independent but strictly related to the specific experimental conditions (17O water enrichment, temperature, and contact time).

5. NATURE AND TOPOLOGY OF SINGLE METAL BINDING SITES IN ZEOLITES: THE ROLE OF 3D ORBITALS

As outlined in the previous section, zeolites provide an ideal platform for the stabilization of single (transition) metal ions at sites, whose nature depends on the zeolite structure, Si/Al and metal/Al ratios. By controlling these parameters, single metal sites can be engineered prompting metal-loaded zeolites toward a number of important catalytic transformations.43 Copper- and vanadium-exchanged zeolites are relevant examples. In this case, the metal–oxide interaction involves the metal 3d orbitals, and 17O hfc measures the σ- and π-contribution to the chemical bond. During catalysis, Cu and V
cycle through paramagnetic states with complementary electronic configurations, namely, Cu$^{2+}$ (3d$^9$) and V$^{4+}$ (3d$^1$). The siting of both elements over the large internal surface of the zeolite is primarily driven by electrostatic interactions brought about by the Al$^{3+}$ distribution in the framework, while the fine details of the electronic structure arise from the favorable interactions between the metal 3d orbitals and the oxide frontier orbitals.

Cu$^{2+}$ species in dehydrated zeolites adopt an unsaturated square planar coordination in the proximity of two framework aluminum ions, that act as charge compensating agents (Figure 4a,b).

Quantitative analysis indicate Cu$^{2+}$/Cu ratio of 0.60

Figure 4. (a) Periodic model for single Cu atoms docked on CHA. (b) CW-EPR spectrum of single Cu ions on CHA. (c) $^{17}$O ENDOR spectra of single Cu ions on $^{17}$O enriched CHA. (d) Periodic model for single VO$^{2+}$ ions docked on H-ZSM-5. (e) CW-EPR spectrum of single VO$^{2+}$ ions on H-ZSM-5. (f) $^{17}$O HYSCORE spectrum of VO$^{2+}$ ions on $^{17}$O enriched H-ZSM-5. The level of $^{17}$O enrichment at the metal site is estimated to be ≈70% in analogy with Zn/ZSM-5. Panels a, b, and c adapted with permission from ref 4. Copyright 2021 the Authors. Published by Springer Nature under the terms of the Creative Commons CC BY license (CC BY 4.0). Panels e and f reproduced with permission from ref 37. Copyright 2020 Elsevier.

Figure 5. (a) Model of the (100) surface of TiO$_2$ anatase. (b) Pulsed EPR spectrum and (c) $^{17}$O ESEEM spectrum of Ti$^{3+}$ at the surface of anatase. (d) Model for single VO$^{2+}$ ions adsorbed on the (100) surface of anatase. (e) CW-EPR spectrum surface (black experimental and red simulated spectrum) and (f) $^{17}$O HYSCORE spectrum of single VO$^{2+}$ ions on $^{17}$O enriched on anatase (100). Panels a, b, and c adapted with permission from ref 2. Copyright 2011 American Chemical Society. Panels d, e, and f reproduced with permission from ref 32. Copyright 2022 Elsevier.
in the dehydrated material. The fine details of the metal coordination structure and the location of the Al in the framework play a crucial role in modulating the catalytic activity but are notoriously difficult to determine. We demonstrated that $^{17}$O EPR provides a robust handle for their quantification. ENDOR experiments performed on Cu-exchanged zeolites with Chabazite (CHA) and ZSM-5 (MFI) topology enriched in $^{17}$O show $^{17}$O coupling on the order of 60 MHz, similar to those observed in the case of Zn$^{2+}$ (Figure 4c) and characteristic of $\sigma$-bonding. Quantum chemical analysis of the spin density distribution shows that the $^{17}$O hfc is very sensitive to the local structural deformations induced by nearby framework Al ions, whose location can be pinpointed with accuracy.4

Similar sating sites stabilize $V^{4+}$ species in ZSM-5 (Figure 4d), in the form of isolated vanadyl ions as revealed by CW-ENDOR (Figure 4e). However, $^{17}$O HYSCORE spectra (Figure 4f) detected only a minute ($\approx 7$ MHz) $^{17}$O hfc with framework oxide ions, which is nearly 1 order of magnitude smaller than the one recorded for Zn$^{2+}$ and Cu$^{2+}$ in the same system. In this case the small $^{17}$O hfc is not related to a reduced covalent character with respect to Cu$^{3+}$ and Zn$^{2+}$ but reflects the fact that the unpaired electron is localized in a nonbonding $\sigma$ orbital and the measured $^{17}$O hfc weighs the degree of metal—oxygen $\pi$-bonding.

6. SINGLE METAL CENTERS WITH 3d$^1$ ELECTRONIC CONFIGURATIONS ON THE SURFACE OF REDUCIBLE OXIDES

While alkali metal atoms bind on the surface of insulating oxides (MgO) through a polarization interaction (see section 4), on the surface of reducible oxides such as TiO$_2$ they spontaneously ionize and forfeit any parentage in the electronic states of the gas-phase alkali atoms. The released “excess electrons” reduce Ti$^{4+}$ forming paramagnetic Ti$^{3+}$ ions, which can be stabilized either in the bulk or at the surface (Figure 5a). $^{17}$O EPR of TiO$_2$ anatase selectively enriched at the surface provided evidence for surface localization of the Ti$^{3+}$ species (Figure 5b,c). The small width of the $^{17}$O ESEEM signal is compatible with a maximum hfc of $\approx$3 MHz (Figure 5c). When dealing with solid-state semiconductors, it is instructive to benchmark the magnitude of the measured hfc against corresponding molecular complexes to gauge the extent of the wave function delocalization. For instance, the fully localized [Ti(H$_2$O)$_8$]$^{3+}$ yields a $^{17}$O hfc of 8 MHz, which is also similar to that measured for the strongly localized Ti$^{4+}$ in the bulk of Ti$^{4+}$ rutile. The scenario is dramatically different when a transition metal ion with the same 3d$^1$ electronic configuration such as V$^{4+}$ is deposited on the surface of TiO$_2$ (Figure 5d,e). This is the observed $^{17}$O HYSCORE spectrum (Figure 5f) characterized by cross-peaks separated by approximately 7 MHz corresponding to a hfc comparable to those observed in VO/ZSM5 and reported for [VO(H$_2$O)$_8$]$^{3+}$ molecular complexes when the unpaired electron is fully localized. This comparison illustrates the profound difference in the electronic structure of an atom at the surface, i.e., part of the lattice (Ti$^{3+}$, Figure 5a) versus an atom deposited on the surface (V$^{4+}$, Figure 5d). The intrinsic differences between these two cases should always be considered carefully, when discussing the electronic structure of metals on oxides and surfaces in general.

7. INTERFACIAL COORDINATION CHEMISTRY OF SINGLE METAL ATOMS AND IONS

The examples presented in the previous sections highlight the role of $^{17}$O as a particularly interesting target nucleus to study the metal—oxide interaction. To extract meaningful results, the measured hfc parameters need to be interpreted in the light of some knowledge of the electron wave function as obtained at...
different levels of accuracy in the frame of electronic structure
theory.\(^8\) The use of simple interpretative models such as ligand
field theory provides, however, a great deal of insight allowing
us to establish sound correlations between classical coordina-
tion chemistry and the bonding of transition metal ions at
surfaces. The properties of single paramagnetic atoms on oxide
surfaces may be interpreted in a general way, considering that
the unpaired valence electron does not materially affect the
binding process but rather represents a convenient probe to
measure the degree of interaction between the metal and the
oxide adsorption site. A simplified orbital correlation diagram
for the cases discussed in this Account, i.e., 3d\(^+\), 3d\(^0\) and 4s\(^+\)
valence electron configurations, captures the essence of the
problem (Figure 6). In the case of surface vanadyl ions
(sections 5 and 6), the local geometry can be described in
terms of a square pyramid with ideal C\(_{4v}\) symmetry (Figure 6a).
Under these circumstances, the unpaired electron of the V\(^{4+}\)
ion (S = 1/2, 3d\(^3\)) is located in a vanadium 3d\(_{xy}\) orbital
(singly occupied molecular orbital, SOMO) with nonbonding
\(\sigma\) character and the weak \(\pi\)-interactions with framework O
ligands are responsible for the small (\(\approx 7\) MHz) \(^{17}\)O hfc. In
the case of Cu\(^{2+}\) (S = 1/2, 3d\(^3\)) the SOMO is the \(\sigma\)-antibonding
orbital contained in the CuO\(_2\) square plane (Figure 6b), in
which the Cu 3d\(_{x^2−y^2}\) orbital is combined out-of-phase with the
2p orbitals of O framework ligands. In this case the \(^{17}\)O hfc
(\(\approx 60\) MHz) is a direct measure of the degree of covalency in
the Cu–O bond and crucially depends on the local structure
distortion (bond lengths and angles).

In a similar fashion for the 4s\(^+\) elements (K\(^+\) and Zn\(^+\)), the
unpaired electron is allocated in a SOMO consisting of the
out-of-phase combination of the metal 4s orbital and the 2p
orbitals of coordinating O framework ligands (Figure 4c).
In general, regardless of the atom considered, there is little
electron transfer at the boundary between the metal and the
surface of nonreducible oxides like MgO or zeolites (i.e., the
unpaired electron is largely localized in the metal orbitals), but
the fine details of the bonding interaction, crucially depend on
the chemical nature of the substrates. In the case of the basic
and ionic MgO, the metal–oxide interaction is dominated by
strong polarization, while in the case of the isoelectronic Zn\(^+\)
bound to the acidic and covalent ZSM-5 in a structurally
similar surface site, the bond has a non-negligible covalent
character, as revealed by the spin density sharing between the
metal and the support. A completely different situation occurs
for a reducible oxide such as TiO\(_2\). In this case neutral metal
atoms (K) are fully ionized and the released electrons localize
in the empty 3d orbitals of Ti\(^{4+}\) ions. The use of surface
selective \(^{17}\)O enrichment allows us to monitor the fraction of
electrons migrating to the bulk and those remaining at the
surface. Moreover, the small \(^{17}\)O hfc indicates a significant
delocalized character of the wave function of surface Ti\(^{4+}\)
ions in anatase, a situation remarkably different from the rutile
polymorph.

8. CONCLUDING REMARKS

Numerous experimental and theoretical studies aimed at a
better understanding of the unique properties of single metal
atoms and ions on oxide surfaces are currently being performed.
Our studies demonstrate that \(^{17}\)O EPR can be a
unique source of information on the structure and bonding
interactions of open-shell single metal atom species. This is
particularly important in cases of structural disorder often
encountered in heterogeneous catalysts where the selective
information from \(^{17}\)O EPR can be vital since other, more
established structural techniques are not able to provide the
same atomic-scale insight. We illustrated some of the guiding
principles for a selective and atom-economic \(^{17}\)O isotopic
enrichment of oxide surfaces and the application of EPR
techniques to unravel fine details of the metal–oxide
interaction. The chosen examples exemplify the role of the
surface as a solid solvent whereby, depending on the oxide
characteristics (acidity, basicity, reducibility), metal atoms or
ions can be described in term of polarized atoms maintaining a
recognizable parentage to gas phase species (alkali metals on
MgO), coordination complexes (e.g., transition metal ions in
zeolites), or ionized fragments (alkali metals on TiO\(_2\)). The
role of the metal support in modifying the electronic structure
of single atoms on surfaces is highly system-dependent. The
oxide support can affect the oxidation state of the adatom,
stabilize unusual oxidation states and coordination geometries,
or promote rearrangements of the orbital energy levels. Under
all circumstances, the detection of \(^{17}\)O hfc is key to the
understanding of the substrate-dependent changes in the
electronic structure of supported single metal atoms on oxides,
which are ultimately responsible for their unique catalytic
properties. The level of structural information that can be
obtained from \(^{17}\)O hfc and hyperfine techniques in general
provides a powerful tool to help quantify and ultimately tune
the multiple features required to design efficient single-metal
catalysts, such as well-tailored electronic and geometric
structure, high stability to sintering or leaching, and sufficient
and uniform single site distributions. We expect this approach
to be extended beyond the study of metal-oxide based catalysts
to other substrates such as two-dimensional carbon-based
hosts and other layered materials, where the most favorable
coordination sites are usually provided by N, O, S, or P. Also,
for this emerging class of materials, selective isotopic
enrichment in conjunction with magnetic resonance techni-
cques can provide unique opportunities to develop an atomistic
understanding of the highly synergistic interactions between
metals and supports that are the basis of unique chemical
reactivity and catalytic performances of single-atom catalysts.

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Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. CRedit T: Enrico Salvadori data curation (equal), formal analysis (equal), investigation (equal), resources (equal), writing-review & editing (lead); Paolo Cleto Bruzzese data curation (equal), software (lead), writing-review & editing (equal); Elio Giamello validation (equal), writing-review & editing (equal); Mario Chiesa conceptualization (lead), funding acquisition (lead), methodology (lead), resources (equal), supervision (lead), writing-original draft (lead).

Notes
The authors declare no competing financial interest.

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Elio Giamello is Emeritus Professor at the University of Torino. His scientific interests revolve around the surface chemistry and photochemistry of metal oxides investigated, in particular, by Electron Paramagnetic Resonance spectroscopy.

Mario Chiesa is Full Professor of Inorganic Chemistry at the University of Torino. His research interests are broadly based in the fundamental understanding of open-shell electronic structure, with applications ranging from catalysis to quantum information science.

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