

EPR Study of the Surface Basicity of Calcium Oxide. 1. The CaO–NO Chemistry

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The surface basic sites at the surface of calcium oxide have been explored following the interaction of nitric oxide with the solid by EPR. Various paramagnetic species are formed depending on the pressure of the gas contacted with the solid. In the initial steps of the interaction, a small amount of a NO_3^{2-} species is formed probably because of the presence at the surface of “anomalous” peroxy or peroxo-like groups. For higher NO pressures, four types of NO_2^{2-} surface species characterized by distinct values of the g and hyperfine tensors are formed by addition of the neutral molecule to basic O^{2-} sites of the surface. The process involves a considerable rearrangement of the spin distribution with respect to the NO molecule with a net decrease of the electron spin density on the N atom. The number of basic sites involved in this interaction is very low and amounts to a value in the range of 0.25–0.5% of the whole surface. These active sites are low coordination sites present at morphological defects of the polycrystalline solid. The concentration of the basic sites is 25 times greater than that of the corresponding sites on MgO thus confirming the higher overall basicity of CaO with respect to magnesium oxide. The surface activity shown by MgO and consisting in a low energy interaction of Lewis acid sites with the NO molecule is, on CaO, totally suppressed.

1. Introduction

The surface chemistry of calcium oxide is far less investigated than the that of the isostructural magnesium oxide, the most known among the alkaline-earth oxides. MgO in fact, because of its simple structure (NaCl), its high ionicity, and its relatively simple morphology, has become in the past two decades a sort of playing ground for groups active in the surface science of oxides^{1–3} (single-crystal faces or thin layers), in surface chemistry (polycrystalline materials),^{4–6} and in theoretical chemistry.^{7–10} The structure of real MgO surfaces, their rich defectivity, and the chemical reactivity of low coordination surface ions are progressively becoming familiar to a number of researchers. The same does not hold for CaO although this oxide finds some applications in the field of automotive exhaust treatments.¹¹

The only remarkable debate involving the surface chemistry of CaO that appeared in the literature in recent years concerns the discussion about its basicity in comparison to that of MgO. Tanabe and co-workers^{12–14} showed in a series of experimental papers that CaO is more active than MgO in the conversion of benzaldehyde into benzyl benzoate and demonstrated that the order of base strength in the group of alkaline earth oxides is $\text{BaO} > \text{SrO} > \text{CaO} > \text{MgO}$.

The reason for the different surface basicity between CaO and MgO has been analyzed in details by Pacchioni et al.¹⁵ by means of ab initio cluster model calculations and rationalized on the basis of simple electrostatic arguments. The authors explain the different basicity and chemical reactivity of the two oxides considering the different Madelung potential at the two surfaces. The O^{2-} ion is in fact unstable in the gas phase where it dissociates into $\text{O}^- + \text{e}^-$ and exists in ionic solids such as alkaline-earth oxides because of the effect of the Madelung

potential. Thus, a reduced Madelung potential implies a reduced stability of the oxide anion. The Madelung potential is different at different surface sites, depending on the Madelung constant of the site which in turn is a function, for a given lattice structure, of the coordination degree of the anion in question and of the lattice constant. CaO has the same cubic structure as MgO but a larger lattice constant ($r_{\text{CaO}} = 2.399 \text{ \AA}$, $r_{\text{MgO}} = 2.106 \text{ \AA}$). As a result, the electron cloud of an O^{2-} ion having a given coordination on CaO is more spatially diffuse compared to that of the corresponding ion in MgO and can overlap better with the orbitals of the incoming molecule explaining the higher reactivity and the increased basicity.

The activity of our laboratory in recent years has been mainly devoted to understand the surface of polycrystalline MgO with particular attention to (i) the structure and properties of surface vacancies,^{4,5} (ii) the interaction with metals,^{16–18} and (iii) the properties of low coordination surface ions.¹⁹ We have mainly employed in our activity the electron paramagnetic resonance (EPR) technique which revealed particularly suited to describe, by means of various paramagnetic probes, the aforementioned points (i–iii). A part from a couple of papers respectively devoted to surface color centers²⁰ and to H_2 – D_2 isotopic substitution on CaO²¹ this oxide has not been thoroughly investigated in our laboratories till the end of the 1990s.

We start with the present paper to report about the surface chemistry of CaO and about its similarities and its differences with respect to that of MgO. As it will be seen in the following, though strong analogies between the two oxides are easily observed, the higher basicity of CaO shows up in terms of a specific reactivity.

In the present paper, we will describe the reactivity of the CaO surface with nitric oxide. The interest for the interaction of NO with CaO is 2-fold. NO is a component of the automotive exhaust, and thus, understanding its reactivity with CaO is important to increase the knowledge on catalytic and noncata-

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lytic devices for the exhaust treatment. Second, NO is a paramagnetic molecule which coordinates upon a number of surface cations giving rise to EPR signals whose features can be related to the electric field exerted by the adsorption site. The chemistry of NO on MgO is relatively well-known. Very few extremely reactive basic O^{2-} ions give rise to a surface NO_2^{2-} paramagnetic compound, whereas the large majority of the surface weakly adsorbs NO in dimeric diamagnetic moieties which have been identified by IR spectroscopy.^{22,23} In the middle of these two extremes three well-defined families of surface cations bind NO at low temperature in monomeric paramagnetic form with the assistance of the nearby surface anion. For these particular sites, the NO molecule acts as a weak basic ligand whose electron density is slightly polarized by the surface electric field. The NO-surface interaction energy, in such a case, is higher than the dimerization energy so that the adsorption occurs in monomeric form. The NO molecule thus monitors three well-defined families of highly exposed, reactive sites two of which are also active in the surface heterolytic splitting of the hydrogen molecule.²⁴

As it will be shown in the following of the present paper, the CaO surface exhibits, as expected on the basis of theoretical calculations,¹⁵ a more basic character than that of MgO. Furthermore, new particular features, not observed on MgO, are observed on CaO allowing an original insight into unexpected properties of the surface chemistry of this ionic oxide. A second paper of this series will deal with the dissociation of alkanes on the same surface.

2. Experimental Section

The experiments were carried out using CaO obtained via slow thermal decomposition of commercial high-purity CaCO_3 (ex- Aldrich). The activation of the sample, to obtain a thoroughly dehydroxylated surface, was performed at 1170 K under a residual pressure of 10^{-5} mbar. The surface area of the resulting oxide is $83 \text{ m}^2 \text{ g}^{-1}$. Traces of Mn^{2+} ions in the bulk of CaO are however practically unavoidable and produce an EPR signal with the typical manganese sextet centered nearby the free electron g value. The signal will always appear in the EPR spectra and has been used as internal standard for g values calibration.

High purity ^{14}NO (Matheson) and ^{15}NO (Icon Service) have been used carrying out all of the experiments.

X-band EPR spectra were recorded at room temperature and at 77 K on a Bruker EMX spectrometer operating at 100 kHz field modulation. The EPR computer simulations were obtained using a program derived from the SIM14S (QCPE) adapted for personal computers.

3. Results

The interaction of NO with MgO was investigated in the past^{22,23,25} and recently revisited by some of us¹⁹ using both experimental techniques (EPR, thermal desorption, and FT-IR) and quantum chemical modeling. It is however useful, in the context of the present paper, to briefly remind the main phenomena taking place upon the NO-MgO interaction. Very few sites at the surface of MgO are capable of a strong interaction with the NO molecule. These are basic O^{2-} sites capable to form a sort of NO_2^{2-} triatomic paramagnetic species, first observed by Lunsford using EPR, by reaction with the NO molecule according to

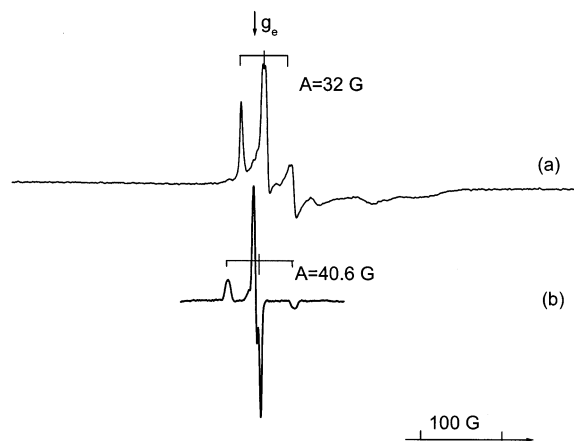
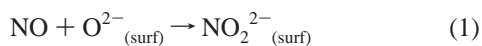


Figure 1. EPR spectra of (a) ^{14}NO physisorbed on MgO at 77 K and (b) chemisorbed ^{14}NO on MgO. Spectrum taken at 77 K after removal of physisorbed and gas-phase NO.

As found by quantum chemical modeling¹⁹ in this species (a radical anion called hereafter species M2 where M stands for magnesium), the two N–O bonds in NO_2^{2-} are not equivalent, but both lengths are in the range typical of chemical bonding, and the N–O distance of the free NO molecule is remarkably increased upon interaction with the surface. Furthermore, the spin density distribution in the surface radical anion is considerably altered with respect to that in the unperturbed NO. All of these facts suggest that the process schematically described by reaction 1 is a true chemical interaction between basic oxygen sites at the surface and the incoming NO molecule acting as a Lewis acid. Nitric oxide, however, is not known as a typical Lewis acid oxide like, for instance, CO_2 and SO_2 which unselectively react with a large number of O^{2-} ions at the surface of alkali-earth oxides, and in particular of CaO. NO reactivity on MgO according to reaction 1 is limited to a few highly basic sites, and the formation of NO_2^{2-} is thus diagnostic of the existence of such sites at the surface. The described interaction takes place at room temperature and no other interaction is observed for the NO-MgO system until the temperature is lowered at 77 K. In such conditions, the surface is actually covered by physisorbed NO molecules in dimeric diamagnetic form,^{22,23} but for a limited number of low coordination surface ions, single NO molecules are polarized by the ionic field to form monomeric weakly bound adducts also observed by EPR (Species M1).¹⁹ For the monomeric species, the energy of the NO-surface interaction is higher than the dimerization energy. In the monomeric adduct, the NO molecule maintains its typical bond length and spin distribution. The EPR spectra of species M1 and M2 are shown in Figure 1 parts a and b, respectively. The spectrum of species M1 is the typical spectrum of a 11-electrons π radical in adsorbed form and is characterized by the presence of three rhombic species with a $g_{xx} \approx g_{yy} > g_{zz}$ value corresponding to three distinct surface sites capable of a different degree of polarization of the adsorbed NO molecule.¹⁹ The three species have similar g_{xx} and g_{yy} and different g_{zz} , the last parameter being connected to the extent of polarization. A rough quantitative estimation of the various species performed comparing the intensity of EPR spectra with the results of adsorption measurements indicates that the surface coverage corresponding to NO in monomeric form (species M1) is between 0.5% and 1% of the surface and that of species M2 is 2% only of the former one. Although species M2 is irreversibly formed at low temperature, species M1 is a weakly bound reversibly adsorbed species, and NO is readily desorbed by increasing T or reducing the gas pressure.

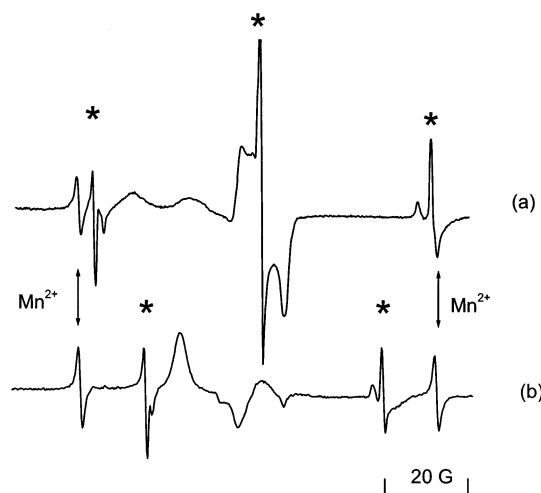
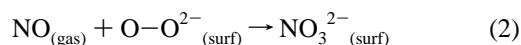


Figure 2. EPR spectra recorded at 77 K of (a) 0.5 mbar of ^{14}NO adsorbed on CaO and (b) the same experiment with ^{15}NO .

The interaction of NO with CaO has been followed by EPR with the same criteria adopted for MgO, i.e., starting from very small doses of the gas at room temperature, increasing the NO pressure and eventually lowering the temperature to detect the weaker interactions.

For a very small dose of NO (0.5 Torr equilibrium pressure), the EPR spectrum shown in Figure 2a is observed which is characterized by the three narrow lines marked with an asterisk and corresponds to a species not observed on MgO (species C1, where C is for calcium). We will discuss later the other broader features observed in the spectrum as they are due to a species whose intensity increases at higher pressure. Species C1 signal is basically an axial signal with the two g values very close one to the other ($g_{\perp} = 2.0048$ and $g_{\parallel} = 2.0044$) which is split in a triplet because of the interaction of the unpaired electron with one N nucleus (^{14}N , $I = 1$). The hyperfine tensor also is slightly axial ($A_{\perp} = 41.8$, $A_{\parallel} = 37.3$), and this allows the observation of the resolved parallel and perpendicular components at the external wings of the spectrum. The previous interpretation is supported by the results obtained using ^{15}NO as shown in Figure 2b. The triplets, in fact, are substituted by doublets centered at the same g values. The full set of spin-Hamiltonian parameters of the signal corresponding to species C1, obtained by computer simulation of the spectra, are reported in Table 1. These parameters are in relatively good agreement with those found for the NO_3^{2-} species in irradiated crystals of KCl and KNO_3 .²⁶ In fact, the Fermi contact term (a_{iso}) for NO_3^{2-} is about 40 G and the g values very close to the free spin value (2.0023) like for the C1 species (for the sake of comparison, the parameters of NO_3^{2-} in irradiated crystal are also reported in Table 1). The difference of C1 from the radical in irradiated ionic crystals mainly resides in the dipolar term of the hyperfine interaction which is, in the case of C1, smaller than in the mentioned ones. To the best of our knowledge, the surface adsorbed NO_3^{2-} radical anion was never observed before. The formation of such species by adsorption of NO on CaO requires us to admit the presence at the CaO surface of small amounts of peroxy or peroxo-like groups. In this case the reaction should be



The particular nature of surface radicals such as NO_2^{2-} or NO_3^{2-} (which are not well defined chemical entities isolated in a host matrix but are built up by reaction of an incoming molecule

and one or more ions belonging to the solid) can explain the discrepancies between the spin-Hamiltonian values of species C1 and those of its counterparts in irradiated solids. The surface species could be significantly different from the matrix isolated radical just because of the deep interactions that can occur between the surface species itself and the whole solid to which it is bound particularly in terms of spin density delocalization.

The hypothesis of the presence, at the surface of CaO, of surface peroxides leading to reaction 2 is in agreement with other evidences, namely, the interaction of oxygen at the surface of bare, activated CaO,^{27–30} which, in its early stages, leads to the formation of ozonide O_3^- radicals whose formation cannot be explained without considering the presence of small amounts of surface entities different from the oxide O^{2-} ions. Though the number of sites involved in reaction 2 is very small, this finding is important as it introduces a first differentiation between MgO and CaO. Although the former is known as a stoichiometric model oxide exclusively composed by Mg^{2+} and O^{2-} ions, the presence of other kinds of surface oxygen ions on CaO, inferred on the basis of the present results, introduces the idea of a minor but interesting deviation from stoichiometry. This point is currently under investigation in our laboratory. In particular, our attention points to ascertain whether the possible presence of traces of aliovalent impurities (even in high purity starting materials) could alter the surface stoichiometry of calcium oxide.

When the NO pressure at room temperature is increased, the features of species C1 disappear and are substituted by the spectrum reported in Figure 3 together with its computer simulation. The spectrum is due to the presence of two akin species (C2 and C2') both containing a single N atom. Each signal displays the rhombic g tensor with the three principal values very close one to the other and the A tensor with one dominating component (33G and 38G for the two species) and the two remaining components very small and practically unresolved. The spectrum is strictly similar to that of species M2 reported in Figure 1a and can be confidently assigned, as in that case, to a NO_2^{2-} species formed according to reaction 1 involving the most basic oxide ions present at the surface. The spin-Hamiltonian parameters of the C2 and C2' species are reported in Table 1 with those of the analogous species in irradiated crystals. Despite the differences between MgO and CaO, the parameters of M2 and C2 are very close one to the other as expected for this kind of 19-electrons, triatomic radicals which are not very sensitive to the surface electric field.³¹ The disappearance of the signal of species C1 (which is isoelectronic with the ozonide O_3^- ion) is probably due to the reaction between this species and gas-phase NO molecules leading to more stable surface (diamagnetic) nitrites:

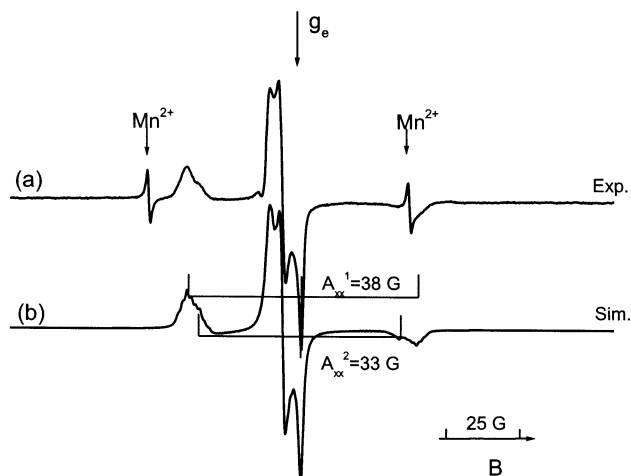
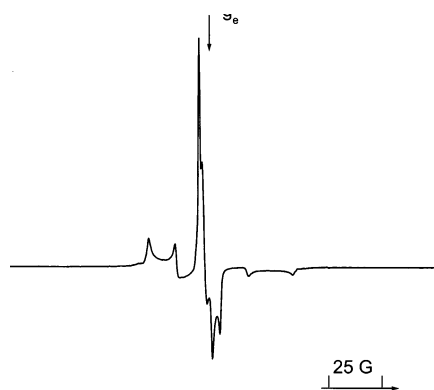


Species C1 could thus be considered a sort of unstable intermediate in the surface oxidation of NO to NO_2^{2-} . The whole reaction path, in any way, should be further investigated monitoring also the diamagnetic species formed at the surface or in the gas phase.

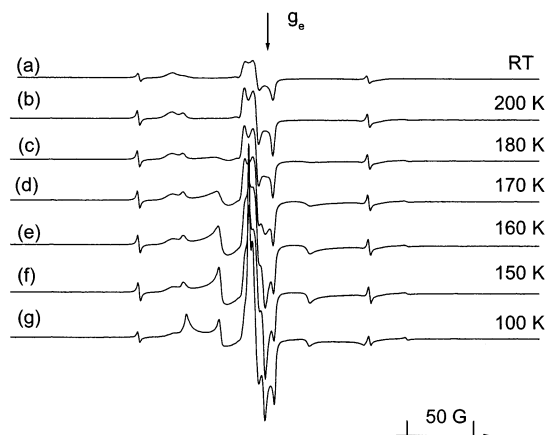
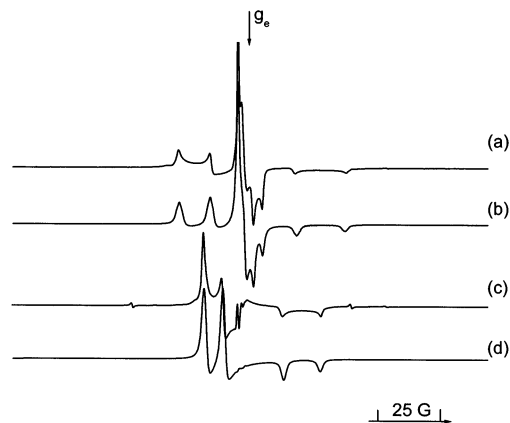
Species C2 and C2' are the only two paramagnetic species stable at room temperature upon adsorption of NO, and at this temperature, they are irreversibly bound at the surface because the intensity of their EPR spectrum remains unaffected by removing the gas phase. After the disappearance of species C1 and the formation of species C2 and C2', the EPR signal remains stable with time and NO pressure indicating that the system is now in equilibrium.

TABLE 1: Spin-Hamiltonian Parameters of the Species Reported in the Paper

species	g tensor			A tensor (G)				ref
	g_{xx}	g_{yy}	g_{zz}	a_{iso}	B_{xx}	B_{yy}	B_{zz}	
C1	2.0048	2.0048	2.0044	+40.3	+1.5	+1.5	-3.0	this work
NO ₃ ²⁻ in crystal matrix	2.0068	2.0068	2.0020	+40.8	-10.3	-10.3	+20.7	26
C2	2.0033	2.0093	2.0069	+11	+22	-11	-11	this work
C2'	2.0029	2.0091	2.0066	+13	+25	-13	-13	this work
C3	2.0023	2.0080	2.0075	+11.3	+21.7	-10.8	-10.8	this work
C3'	2.0044	2.0080	2.0064	+6.2	+11.3	-5.7	-5.7	this work
NO ₂ ²⁻ in crystal matrix	2.0038	2.0099	2.0070	+14.3	16.6	-9.3	-7.3	26

Figure 3. EPR spectrum after adsorption of 5 mbar of ¹⁴NO on CaO (a) experimental spectrum and (b) simulated spectrum.Figure 4. EPR spectrum, recorded at 77 K, after adsorption of 25 mbar ¹⁴NO on CaO at room temperature

Like in the case of MgO, other paramagnetic species can be observed by lowering the adsorption temperature to 77 K. Figure 4a reports the spectrum recorded at this temperature under 25 Torr NO. In such conditions, the features of C2 species are completely overwhelmed by a more intense, new EPR spectrum because of weakly bound paramagnetic species. This is illustrated by Figure 5 where the formation of the new spectrum is followed by lowering the temperature under NO pressure. At 250 K, C2 and C2' are the only species present at the surface, and the formation of the new entities starts at about 170 K. At 100 K, the spectral profile has assumed its final form. All of the process is completely reversible, and the initial situation is restored by increasing temperature indicating the weak nature of the bond between the surface and the new adducts. Surprisingly, however, the spectral features of the weakly bound species on CaO are not those of the slightly perturbed NO molecule observed on MgO (M1, spectrum of a diatomic π radical) but are much more similar to those of the NO₂²⁻ triatomic radical (M2, C2, and C2') formed by reaction of NO with an oxygen

Figure 5. EPR spectra recorded at various temperatures after adsorption of 25 mbar ¹⁴NO at room temperature and then lowering the temperature to 100 K.Figure 6. EPR spectra of weakly adsorbed NO₂²⁻ species (C₃ and C_{3'}) recorded at 77 K under. (a) ¹⁴NO experimental spectrum, (b) simulation, (c) ¹⁵NO experimental spectrum, and (d) simulation.

ion of the surface (1). The outer wings at high field, for instance, are not low value g tensor components, like in the case of M1 species. This is demonstrated by the spectrum recorded using ¹⁵NO which is compared in Figure 6 with the corresponding spectrum recorded under ¹⁴NO. The spectral features at high field in fact have moved toward the center of the spectrum unambiguously indicating that they belong to a N hyperfine structure. Despite the apparently simple structure of the new spectrum, the simulation of its profile (Figure 5b) has not been easy and is not yet completely satisfactory. The best result of the computer simulation was obtained with the hypothesis of the presence of two different species (C₃ and C_{3'}) having a structure of the spin Hamiltonian strictly similar to that of M2 and C2 but different g and A values (Table 1) and thus amenable again to triatomic NO₂²⁻ type radical ions. The main hyperfine value of the C_{3'} species, however, is quite lower in comparison to the corresponding values observed on the other C species.

The explanation of this fact is not straightforward and, in any case, the discussion of all spectroscopic details is beyond the scopes of the present paper which is essentially devoted to the description of the surface basicity of CaO. An issue, however, could be found considering the possibility of a monoclinic symmetry of the paramagnetic species with noncoincidence of the g tensor and A tensor axes. In such a case, the hyperfine separation observed on the experimental spectrum is not the real one, and a correction should be done provided that the angle between the two tensor axes is known. Investigations concerning this delicate point are still going on in our laboratory.

A rough quantitative analysis of the spectral intensity indicates that the amount of C3–C3' species is about eight times higher than that of C2–C2'.

4. Discussion

The main result of the present investigation consists of the fact that the activity of CaO and MgO in the formation of paramagnetic species by surface reaction with NO presents some analogies but also substantial differences. In fact, in the case of MgO, a weak interaction prevails because of polarization of the NO molecule by the electric field of low coordination surface cations (M1, Figure 1) which act as weak Lewis acid sites. The basic character of the surface with respect to the NO molecule is limited to very few O^{2-} sites (0.01–0.02% of coverage) which react with NO leading to the formation of a NO_2^{2-} type radical anion (M2, Figure 1) irreversibly bound at the surface. The former type of interaction is completely suppressed passing from MgO to CaO where the second type of activity is dominant leading to the formation of four distinct species (C2, C2', C3, and C3') with similar nature. This fact is in complete agreement with the higher basicity of the oxide ions on CaO which has been experimentally observed in various reactions and theoretically described by Pacchioni and Illas,¹⁵ who investigated the interaction of the two surfaces with acidic molecules such as CO_2 and SO_2 . A rough quantitative analysis of the present data confirms this idea. We have evaluated the ratio between the number of basic sites on MgO and CaO per square meter of exposed surface by careful integration of spectra recorded in the same conditions. In particular, we have compared the surface concentration of species M2 in the case of MgO with that of species C2, C2', C3, and C3' on CaO. The basic sites capable of the described reaction with NO per square meter of CaO are about 25 times those observed on the same surface on MgO. Nevertheless, the whole amount of this sites is rather small and lies in the range 0.25–0.5% of the surface coverage. High surface area alkali-earth oxides are made up of cubelets mainly exposing (100) faces. This means that the vast majority of surface ions are those 5-coordinated present at this face which amount to about 90% of the total.³²

The remaining ions (about 10%) are the 4- and 3-coordinated ions having higher reactivity. In this perspective, the strong CaO basic sites reacting with NO, with various degrees of interaction, are between 2.5% and 5% of the whole low coordination ions.

The small amount of basic sites involved in the interaction with NO at the surface of CaO indicates that we are dealing with special sites which have to be found among the highly basic sites with low coordination (4c, 3c) present at the morphological defects of the surface such as steps, edges, kinks, and corners where the low coordination induce a high reactivity.¹⁵

The description derived on the pure basis of the EPR data points to radical species which can be compared, at a first degree of approximation, with the NO_2^{2-} species in irradiated crystal.

TABLE 2: Nitrogen Spin Densities of the Paramagnetic Species

species	spin densities			
	ρ_{2s}	ρ_{2p}	ρ_{tot}	
M1	0.011	0.792	0.803	ref 19
C2	0.020	0.630	0.650	this work
C2'	0.017	0.555	0.572	this work
C3	0.020	0.555	0.570	this work
C3'	0.010	0.280	0.290	this work

The latter one is a triatomic 19-electrons radical ion formed according to the process reported in eq 1. For such kinds of species, the unpaired electron is in a b_1 orbital which is a sort of π antibonding orbital formed by three p atomic orbitals of N and O, respectively, so that a weak isotropic coupling to the nitrogen atom is expected exactly as found in our case for all C2 and C3 species. The perturbation of the NO molecule, as observed by the point of view of EPR, is in all cases quite substantial. To focus on this point, Table 2 reports the spin densities on the N atom for the various species here discussed as deduced by the analysis of the hyperfine tensors. As it can be seen from the table, the formation of a chemical bond between NO and a surface oxygen ion involves the decrease of the spin density on the nitrogen atom. This latter one is about 0.85 in both of the free molecule and the weakly perturbed adsorbed NO (species M1) and progressively falls for the various C2 and C3 species till about 0.3 with consequent higher spin density localization on the oxygen atoms and, possibly, toward the solid.

An original aspect of the findings reported here is that on the same system an entire family of similar but not equal radical species can be formed. This is not completely surprising as the heterogeneity of the surfaces (i.e., the presence of sites with the same chemical nature but different coordination and reactivity) is a well-known phenomenon in surface chemistry and often leads, like in the present case, to the formation of species having basically the same nature but different features.

The truly surprising fact in the present case is, however, that the four species, though quite similar in terms of spin-Hamiltonian parameters (Table 1), have respectively strong (C2 type) and weak (C3 type) interactions with the surface. Remarkably, for species C3 and C3', a substantial rearrangement of the molecular and electronic structure with respect to the NO molecule does not correspond to a strong bonding with the surface. The absence in the radical anion of nuclei, other than nitrogen, with nuclear spin different from zero precludes a further experimental exploration of the spin density of the surface paramagnetic adducts so that the only way to shade further light on this problem is to perform careful theoretical modeling to describe the bonding energy and the spin densities of the species obtained putting NO in contact with various types of surface O^{2-} on CaO in analogy with what done in the NO–MgO case.¹⁹

Finally, it has to be kept in mind that the reactivity described in the present paper is just a fraction (the paramagnetic fraction) of the whole reactivity of NO with the CaO surface. Further investigations are needed to unravel the diamagnetic part which certainly occurs in particular at 77 K. At this temperature in fact, physisorption occurs and all of the surface is probably covered by NO molecules in some diamagnetic form as it happens in the case of MgO. The amount of the observed paramagnetic species observed even at 77 K is in fact rather low and, as discussed before, is far to represent a full monolayer.

5. Conclusions

The surface chemistry of CaO with respect to NO has been followed and compared with that of MgO, monitoring the formation of paramagnetic surface species. The main finding of this investigations can be resumed as follows.

a. A small amount of a NO_3^{2-} species is formed in the early steps of the interaction probably because of the presence at the surface of "anomalous" peroxy or peroxo-like groups (eq 2).

b. The rest of the interaction is substantially amenable to the reactivity of basic oxygen ions with NO to form four distinct types of NO_2^{2-} surface species characterized by distinct values of the g and hyperfine tensors (eq 1).

c. The number of sites involved in this interaction is very low and amounts to a value in the range of 0.25–0.5% of the whole surface ions (or 2.5–5% of the low coordinated ones). These active sites are reasonably low coordination sites present at morphological defects of the polycrystalline solid as, for these sites, a higher reactivity is expected with respect to the most abundant sites present at the terraces. The concentration of the basic sites is 25 times greater than that of the corresponding sites on MgO thus confirming the higher overall basicity of CaO with respect to magnesium oxide. The NO probe has been used in this work as an acidic probe. However, because of its low acidity, this molecule constitutes a probe for very special highly basic sites and its use will remain probably limited to a restricted number of basic oxides.

d. The surface activity shown by MgO and consisting in a low energy interaction of Lewis acid sites with the NO molecule is, on CaO, totally suppressed.

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