

EPR Study of the Surface Basicity of Calcium Oxide. 2: The Interaction with Alkanes

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The present paper reports experimental evidence of the heterolytic dissociation of some saturated hydrocarbons (methane, ethane, propane, and cyclohexane) at the surface of high surface area CaO activated at high temperature. The reaction takes place at RT on particularly basic O^{2-} sites at the surface of CaO. The reaction has been followed via EPR spectroscopy in two distinct ways. The former one consists of monitoring the formation of superoxide radical anions (O_2^-) which occurs when the hydrocarbon and molecular oxygen are coadsorbed at the surface via surface intermolecular electron transfer reaction. The latter one is based on ionization of the negative hydrocarbon fragment upon exposure to UV light with consequent formation of a surface trapped electron (a surface color center known as $F_s(H)^+$) in which the electron is stabilized nearby an hydroxyl OH^- group produced by the hydrocarbon splitting. This latter OH^- group undergoes isotopic exchange transforming in OD^- when contacted with D_2 or CD_4 .

1. Introduction

The low reactivity of alkanes limits their direct use in conversion reactions to form different chemicals. The catalytic transformation of alkanes is relevant, however, to many important industrial process, e.g., steam reforming, combustion, partial oxidation, methanation, Fischer–Tropsch synthesis, and isomerization¹. The methane molecule, for instance, is extremely stable in comparison to other hydrocarbons because of its high ionization energy (1157.8 kJ/mol), low proton affinity (424 kJ/mol), and strength of the C–H bonds (439 kJ/mol).

Most of the studies about methane interaction with the surface have been carried out on transition metals.

Oxides, however, are used in several studies for the methane oxidation to methanol and formaldehyde and for the oxidative methane coupling.^{2–34} There is large experimental evidence that this latter reaction proceeds through a free radical mechanism at the surface of basic oxides, such as MgO, CaO, Sm_2O_3 , and lanthanide oxides,⁵ and there are indications that the rate determining step is the initial hydrogen abstraction from methane by the surface⁶ to produce methyl radicals.^{7,8} The whole mechanism of the reaction is however very complex, and some doubts remain regarding the nature of the surface sites on which hydrogen abstraction occurs and the nature of the C–H bond cleavage (homolytic or heterolytic) that is involved in methyl radical formation.⁹

Among basic oxides, MgO and, though to a lower extent, CaO have been the subject of several studies because they show good catalytic properties in methane oxidative coupling either after some high-temperature activation or when doped with alkaline metals. The most used systems are lithium promoted magnesium oxide Li/MgO and sodium promoted calcium oxide Na/CaO.⁵ The dissociation and the adsorption of the dissociated

hydrocarbon fragments depend on the sites available on the surface. The most active sites for homolytic dissociation are thought to be the electrophilic oxygen species such as O^- , O_2^- , and O_2^{2-} , able to abstract H from RH.^{10–13}

Some authors indicate instead a role also for defective sites such as vacancies, electrons trapped therein, low-coordinated ions steps, and corners as responsible for the hydrogen abstraction.^{12–14}

An alternative possibility for methane activation is the heterolytic C–H bond cleavage occurring on coordinatively unsaturated metal–oxygen pair sites to produce methyl anions, which then subsequently react with oxygen to release methyl radicals.^{15–18} This type of cleavage has been proved to act also in the case of surface oxidation of alkenes and of some aromatics such as toluene¹⁹ on MgO. Because of the very weakly acidic nature of the C–H bonds in alkanes ($pK_a > 50$), sites that are able to heterolytically activate methane and other alkanes (if any) must be much more strongly basic than those capable of promoting the same C–H bond breaking on alkenes and toluene.

The subject of the initial activation of the alkanes on basic oxide surfaces is still matter of discussion and results obtained by different researchers are in partial disagreement.^{17,20,21} It was on one hand reported, for instance, that, at low temperature, MgO does not adsorb methane,^{20,21} but on the other hand, it has been reported that MgO catalysts dissociate CH_4 heterolytically into CH_3^- and H^+ even below room temperature.¹⁷ The basicity of the CaO surface in comparison with that of MgO has been the object of the first paper of this series in which the NO molecule was used as a surface paramagnetic probe.

In the present paper, we investigate by EPR spectroscopy the interaction of some saturated hydrocarbons (methane, ethane, propane, and cyclohexane) with the thoroughly dehydrated surface of bare MgO and CaO in order to unravel the occurrence of heterolytic dissociation at the surface. Two distinct types of experiments have been performed. The former is the hydrocarbon–oxygen coadsorption already adopted for propene and toluene in the past.^{19,22} In this case, the formation and surface

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stabilization of a superoxide radical anion (easily monitored by EPR) is the proof that the heterolytic splitting of a C–H bond has occurred. The latter type of experiment is based on the well-known observation that, on both MgO and CaO, UV irradiation of adsorbed fragments of molecular hydrogen (which is heterolytically dissociated at these basic surfaces) leads to ionization of the anion (H^- in the case of H_2) and formation of surface trapped electrons.^{23–26} The same type of experiment (a sort of photoactivation of the adsorbed fragment) was repeated using the four hydrocarbons above-mentioned, thus extending to the C–H bond the investigation on the H–H bond activation. EPR was used as the high sensitivity of the technique allows to monitor even tiny amounts of paramagnetic species.

In a recent paper by some of us,²⁷ it has been shown that H_2/D_2 exchange takes place on particular surface hydroxyls of CaO and that the phenomenon can be revealed monitoring the changes of the EPR spectra of electrons trapped nearby the OH group. As it has been hypothesized that H–D isotopic exchange reactions among alkanes occur over metal oxide catalysts via heterolytic dissociation of C–H and C–D bonds,^{16,28,29} we have extended the investigation of the OH group reactivity in isotopic exchange²⁷ to the case of methane–deuterated methane.

The present paper is therefore organized as follows. The first part (section 3.1) reports the results obtained by oxygen-hydrocarbons coadsorption on fully dehydrated CaO. Section 3.2 deals with trapped electron centers formation upon irradiation in the presence of hydrocarbons and section 3.3 with the isotopic exchange reactions monitored by means of the surface trapped electrons. A short discussion to compare the basicity of MgO and CaO concludes the paper.

2. Experimental Section

The experiments were carried out with two different alkaline earth oxides.

(a) High surface area MgO was produced by thermal decomposition of $\text{Mg}(\text{OH})_2$ under dynamic vacuum at 523 K for 16 h. Samples were activated at 1073 K (1 h) under dynamic vacuum in order to obtain a totally dehydroxylated surface. The resulting surface area (measured by the B.E.T. method) after this treatment was $\approx 200 \text{ m}^2\text{g}^{-1}$.

(b) Calcium oxide was obtained via slow thermal decomposition of commercial high-purity CaCO_3 (from Aldrich) as already described in a previous paper.²⁴ The activation of the sample to obtain a thoroughly dehydroxylated surface was performed at 1170 K (1 h) under a residual pressure of 10^{-5} mbar. The surface area of the resulting oxide was measured by B.E.T. method and is about $80 \text{ m}^2\text{g}^{-1}$. To allow quantitative evaluations in all experiments, a constant amount of sample was used.

Despite the purity of the starting material, traces of Mn^{2+} ions in the bulk of CaO and MgO are always present and produce an EPR signal with the typical Mn^{2+} sextet centered nearby the free electron g value. The signal always appears in the EPR spectra and has been used as an internal standard for g values calibration.

To produce trapped electrons centers, the activated samples were exposed respectively to H_2 , D_2 , CH_4 , C_2H_6 , C_3H_8 , and C_6H_{12} (100 mbar) and irradiated using a low-pressure mercury vapor lamp (Polymer 401, Helios Italquarz, 400W) for 1 h at 77 K. High purity gases (Praxair) have been used in all 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.

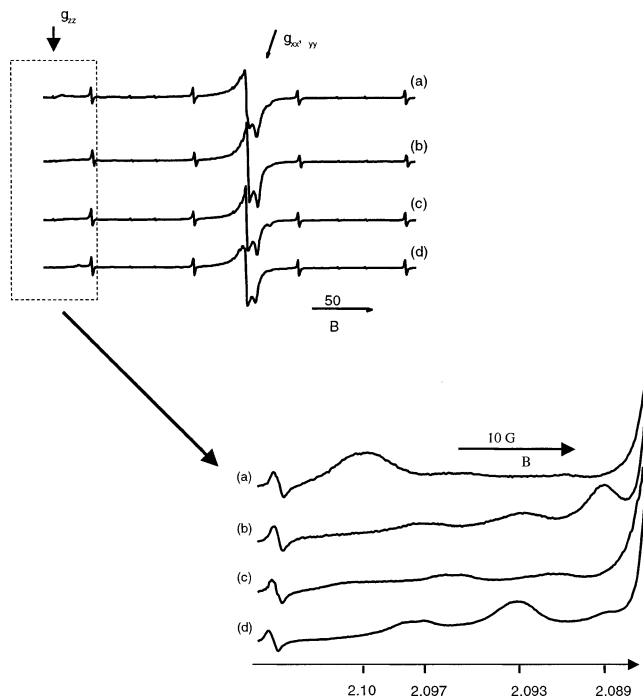


Figure 1. (a) EPR spectra at 77 K of superoxide O_2^- anion obtained by coadsorption on CaO surface of molecular oxygen with (a) CH_4 , (b) C_2H_6 , (c) C_3H_8 , and (d) C_6H_{12} .

3. Results

3.1. Superoxide Formation on CaO by Reaction between Coadsorbed Hydrocarbons and O_2 . The formation of adsorbed superoxide O_2^- ions by coadsorption of oxygen and various hydrocarbons was observed in the case of MgO^{19,22,33} for a series of hydrocarbons including propene and toluene. This finding was discussed on the basis of a SIET mechanism (surface intermolecular electron transfer, vide infra),^{30,31} which eventually leads to the transformation of the hydrocarbon in two oxidized fragments^{32,22} but whose first step is the heterolytic dissociation of a C–H hydrocarbon bond at the surface with formation of an H^+ ion (stabilized as a surface hydroxyl group) and an organic anion. This latter, in turn, is capable of electron transfer to molecular oxygen with the formation of O_2^- . A fraction of these ions start the electrophilic attack to the carbanion, whereas another fraction remains unreacted and stabilized at a surface site of the oxide.³³ The formation of O_2^- is therefore diagnostic of the heterolytic dissociation of the CH bond. The coadsorption at RT of O_2 and methane, ethane, propane, and cyclohexane respectively has been investigated at the activated surface of both MgO and CaO. On MgO, no reaction was observed at room temperature for all saturated hydrocarbons, except for methane which gave an extremely weak EPR spectrum probably ascribable to traces of superoxide. This result cannot be considered fully positive with respect to the C–H bond splitting. In the case of CaO, on the contrary, adsorbed superoxide ions are readily formed by oxygen adsorption at room temperature on the surface in the presence of methane, ethane, propane, and cyclohexane. The EPR spectra observed for these four hydrocarbons are reported in Figure 1 and are all due to adsorbed superoxide ions. O_2^- ($S = 1/2$) is a π radical ion easily detected by EPR spectroscopy when adsorbed at a cationic surface site, the electrostatic field of which removes the degeneracy between the two π^* oxygen orbitals. This leads to an orthorhombic symmetry with three principal g values g_{xx} , g_{yy} , and g_{zz} , the z direction being that of the O_2^- intermolecular axis.³³ The g_{zz} component is very sensitive to the electrostatic field of the

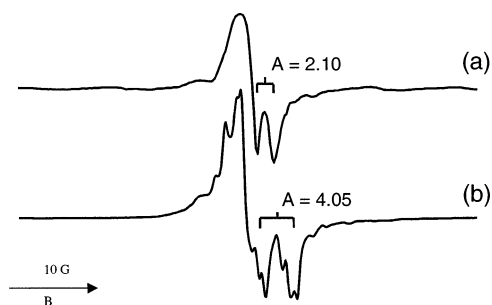


Figure 2. EPR spectra recorded at room temperature of $\text{Fs}(\text{H})^+$ color centers formed on (a) MgO and (b) CaO, by UV irradiation at 77 K of the activated oxides under excess H_2 .

adsorbing cation. The higher the surface electrostatic field, the lower the g_{zz} value.^{22,33–35} The four spectra in Figure 1 are very similar one to each other in the region close to the free electron value (g_{xx} and g_{yy}), whereas they differ in the low field g_{zz} region whose magnification is reported in the second part of the figure. All spectra show several g_{zz} components. This indicates a heterogeneity of adsorbed species with various distinct surface sites involved in superoxide adsorption. Interestingly, the distribution of the species is not the same in all cases but depends on which hydrocarbon has been used in the experiment (see section 4.2). The intensity of the spectra reported in Figure 1 is rather low; however, they are not due to impurities of more acidic molecules in the gas as proven by the absence of spectra when the same gases were contacted with MgO.

Although the quantitative analysis of the phenomena was not among the main goals of the present work, it has to be noticed that the intensities of the four spectra in Figure 1 are close one to the other. This indicates that the small amount of superoxide stabilized at the surface is independent from the nature of the hydrocarbon employed in the experiment.

3.2. Irradiation of Adsorbed Alkanes on CaO. It is well-known that after dehydration of both MgO and CaO at high temperature (1073–1173 K) and UV-irradiation at 77 K in the presence of H_2 the formation of a particular type of surface defect the $\text{Fs}(\text{H})^+$ centers is observed.^{23,24} These centers (belonging to the family of color centers) basically consist in single electrons trapped in a suitable surface trap and are characterized by a magnetic interaction with the proton of a nearby hydroxyl group. This interaction is the origin of a hyperfine doublet with separation of 2.07 G for MgO and 4.05 G for CaO (Figure 2).

If deuterium ($I = 1$) is used instead of hydrogen ($I = 1/2$) during the irradiation with UV light, the center is called $\text{Fs}(\text{D})^+$,^{23,25,36} and an unresolved triplet takes the place of the hyperfine doublet.

Similar experiments were performed contacting the activated surface of MgO and CaO with methane, ethane, propane, and cyclohexane (100 mbar). The interaction between these hydrocarbons and the bare oxide surface does not lead to the formation of any paramagnetic species, and no EPR spectra are observed in this case. However, upon UV irradiation of the solid in hydrocarbon atmosphere, a pale blue color develops in the case of CaO with simultaneous appearance of an EPR signal. The spectra observed for the four hydrocarbons, Figure 3a–d, are quite similar but not equal to that in Figure 2b. They are characterized by the presence of a species, which resonates close to the free-electron g value and which has an axial symmetry and a characteristic doublet hyperfine structure (with a coupling constant of about 4 G) due to the interaction with protons. In analogy with the species obtained in the presence of hydrogen

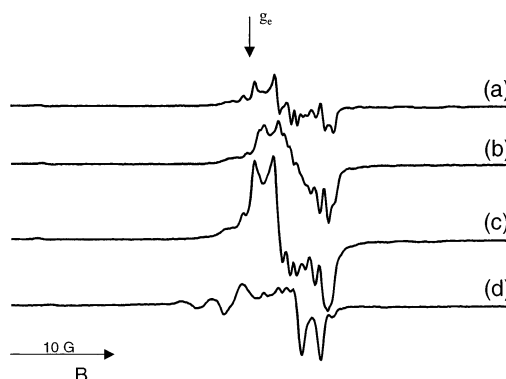


Figure 3. EPR spectra at room temperature of $\text{Fs}(\text{H})^+$ color centers formed on CaO, by UV irradiation at 77 K of the activated oxides under excess (a) CH_4 , (b) C_2H_6 , (c) C_3H_8 , and (d) C_6H_{12} .

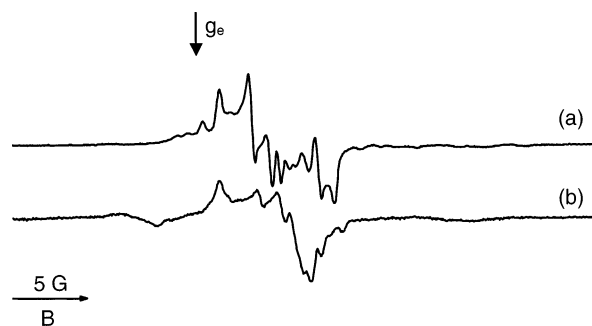


Figure 4. EPR spectra at room temperature of $\text{Fs}(\text{H})^+$ color centers formed on CaO, by UV irradiation at 77 K of the activated oxides under excess (a) CH_4 , (b) CD_4 .

(Figure 2b), exhaustively discussed in the past,^{23,24,36} it is reasonable to assign these species to surface $\text{Fs}(\text{H})^+$ centers. No evidence of color centers has been obtained by irradiation in the presence of the same hydrocarbons at the surface of MgO. The spectra reported in Figure 3a–d appear more complex, however, than that obtained after irradiation in H_2 . The main doublet in the spectrum obtained using CH_4 (Figures 3a and 4a) is transformed into a triplet (Figure 4b) if CD_4 is used. Owing to the reduced magnetic moment of deuterium ($\mu_{\text{H}} \approx 6.5 \mu_{\text{B}}$) the triplet of lines is expected to have a smaller separation (about 0.6 G) than the hydrogen doublet and remains usually unresolved. Beside the main hydrogen hyperfine doublet, however, a multiplicity of satellite lines appears in Figure 4a. This complexity very likely arises only in part from the interaction between the unpaired electron and other hydrogen nuclei belonging to the organic substrate as desumed by comparing part a with part b in Figure 4.

The capability of the various hydrocarbons to form trapped electrons centers upon irradiation is not the same. In particular, the centers formed via propane (Figure 3c) are more abundant than in the other three cases.

3.3. Isotopic Exchange on CaO Electron Rich Surface. As shown by some of us in a recent paper,²⁷ the OH group close to $\text{Fs}(\text{H})^+$ centers on CaO (when the centers are generated by irradiation in hydrogen) undergoes isotopic exchange with D_2 at room temperature. The phenomenon is reversible, and OD groups can react with H_2 restoring the starting situation. The isotopic exchange capability of the surface has been explored also for the centers obtained using hydrocarbons.

Figure 5 shows a series of spectra observed starting from that of $\text{Fs}(\text{H})^+$ generated by UV irradiation in CH_4 and recorded under vacuo (Figure 5a). After 100 mbar of deuterium has been admitted into the cell at room temperature, a dramatic change

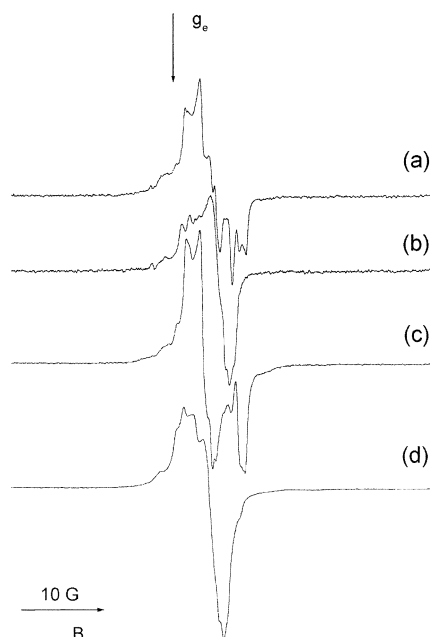


Figure 5. Isotopic exchange: (a) EPR spectra of $\text{Fs}(\text{H})^+$ color centers formed on CaO, by UV irradiation at 77 K of the activated oxides under excess CH_4 , (b) +100 mbar D_2 , (c) +100 mbar $^{13}\text{CH}_4$, and (d) +100 mbar CD_4 .

in the spectrum occurs (Figure 5b). The doublet of lines due to the interaction of the electron with a H nucleus is replaced by the unresolved triplet of lines due to the electron–deuterium interaction, revealing a fast isotopic exchange between the OH group and gaseous D_2 . The newly formed $\text{Fs}(\text{D})^+$ centers are quite stable in vacuo. However the admittance of other 100 mbar of CH_4 into the EPR cell restores completely the $\text{Fs}(\text{H})^+$ EPR spectrum (Figure 5c), showing that the exchange reaction is completely reversible and, more important, that it occurs also using methane instead of H_2 . Finally, the sample was contacted with 100 mbar of CD_4 with formation of the spectrum in Figure 5d which indicates that a $\text{Fs}(\text{D})^+$ center has been formed, again similar to that of spectra shown in Figures 4b and 5b. Summarizing, in the previous sections, it has been shown that irradiation of CaO in the presence of four different hydrocarbons lead to the formation of surface F centers in interaction with a nearby OH group. The surface OH groups are active in the H/D isotopic exchange that can be carried out using either the diatomic molecules (H_2 – D_2) or the hydrocarbon molecules (CH_4 – CD_4).

4. Discussion

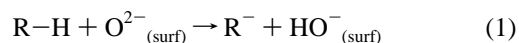
4.1. Mechanism of the Surface Reactions. The first point to be emphasized is the marked difference between MgO and CaO in their behavior toward saturated hydrocarbons. The above-described experiments have indirectly monitored the capacity of the surface of CaO to dissociate heterolitically the R–H bond of some molecules of extremely low acidity which, with the exception of CH_4 discussed before, do not react at all with MgO (see Table 1).

The formation of superoxide anions by the reaction (at room temperature) of the CaO surface with coadsorbed R–H and O_2 without the assistance of UV light can be explained invoking the SIET (surface intermolecular electron transfer) mechanism already established in the case of similar reactions on MgO,^{19,22} whose first step is the heterolytic splitting of the C–H bond. For this reaction, a strong basic site is required which must be

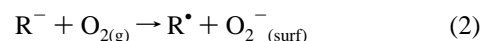
TABLE 1: Acidity Scale of R–H Molecules: pK_a Values in Solution

R–H	R [−]	pK_a	dissociation on MgO	dissociation on CaO	ref
H_2	H^-	35	yes	yes	41
CH_4	CH_3^-	48	borderline	yes	42
C_2H_6	CH_3CH_2^-	50	no	yes	43
C_3H_8	$(\text{CH}_3)_2\text{CH}^-$	51	no	yes	43
C_6H_{12}	$\text{C}_6\text{H}_{11}^-$		no	yes	

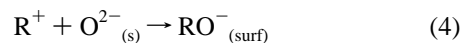
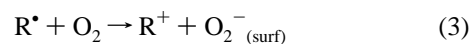
a particular low coordination O^{2-} ion at the CaO surface (vide infra)



The carbanion formed is unstable toward oxygen and transfers an electron to the O_2 originating superoxide anions which are stabilized on suitable Ca^{2+} sites at the surface



The O_2^- EPR signal demonstrates that the heterolytic activation of the R–H (1) has actually occurred. Some authors suggest¹⁶ that the reaction proceeds with the formation of RO^- species according to the following further steps

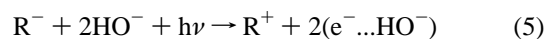


The surface alkoxy group RO^- was not directly observed (for instance by IR spectroscopy) because of its low surface concentration. Its formation is however expected as the acidic R^+ carbocation is a transient species which cannot survive on a basic surface where it reacts according to eq 4.

Not all the steps of the SIET mechanism (involving heterolytic splitting of the hydrocarbon) have been directly documented by the experiments. This was however done in the case of the H_2 – O_2 surface reaction. In this case, the formation of two fragments (H^+ and H^- , respectively) by H_2 adsorption and the simultaneous decrease of H^- and increase of O_2^- concentration upon oxygen exposure were all experimentally documented.³⁷

The similarity of the two reactions (H_2/O_2 , RH/O_2) is strict and the mechanism described by eqs 1–4 can be confidently adopted excluding any role (in the experimental conditions of the present work: bare undoped oxide, room temperature, no irradiation) of the homolytic splitting.

The formation of surface F centers upon irradiation of the adsorbed hydrocarbon is witnessed by the pale blue color assumed by the solid and by the appearance of the typical EPR spectrum and can be explained considering the same initial step reported in (1). Subsequent irradiation in the absence of oxygen causes ionization of the carbanion and formation of a $\text{Fs}(\text{H})^+$ centers according to



where the symbol $(\text{e}^- \dots \text{HO}^-)$ represents a $\text{Fs}(\text{H})^+$ center. This reaction is analogous to the reaction observed for the hydride ion when H_2 is used instead of the hydrocarbon.^{28,29,37} Again R^+ is just a reactive intermediate and reacts with surface oxide ions according to eq 4.

A possible alternative hypothesis is based on the homolytic splitting of the C–H bond entailed by O^- ions formed by the process of charge-hole separation induced in the solid by the UV light. This hypothesis, however, has to be ruled out because

TABLE 2: g_{zz} Values of Superoxide O_2^- Species Formed by Coadsorption of Oxygen and Hydrocarbons (see Figure 1)

R-H	g_{zz} values		
H ₂	2.097		
CH ₄	2.091	2.097	2.102
C ₂ H ₆	2.089	2.093	2.097
C ₃ H ₈	2.091	2.097	2.102
C ₆ H ₁₂	2.089	2.093	2.089

the same electronic process under UV occurs also on MgO³⁸ and no formation of paramagnetic centers has been observed on this oxide. The two types of observed processes (dark reaction with O₂ and photochemical activation) are thus based on the initial proton abstraction from the RH molecule (1) and have to be explained admitting a strong basic behavior of particular O₂⁻ surface sites on CaO. This latter oxide, in particular, results, as expected and as already found investigating the surface chemistry of NO on alkaline-earth oxides,³⁹ more basic than MgO. As discussed by Pacchioni et al., the stronger basicity of CaO with respect to MgO is due to a reduced Madelung potential acting on the O₂⁻ surface ions of the former oxide which increases the instability and, consequently, the reactivity of the ion itself.⁴⁰ The reduced Madelung potential, in turn, is due to the different lattice constant of the two isostructural oxides. The few sites (the intensity of EPR spectra reported in the present work is always quite low) on the CaO surface which give rise to the observed reactivity must have low coordination and are probably three-coordinated sites available at corners and kinks of the cubic microcrystals as the lower the coordination, the lower the Madelung constant, the higher the expected basic reactivity. To have an undirect idea of the basic potential of the sites available on CaO, it is useful to report the acidity of the various molecules involved in the surface reaction (Table 1) in terms of pK_a in solution.

The reason for the use of the solution acidity scale instead of the gas acidity scale is due to the nature of the solid. MgO surface has an effect comparable to that of a solvent cage in stabilizing the anion produced in the dissociation.²¹ Though this value is not completely appropriate to discuss phenomena taking place at a gas-surface interface, it constitutes an indication of the sequence of the acidities of the various molecule involved in the surface interaction. As reminded in the previous sections, the reactivity of methane on MgO was not completely absent, but the spectral intensity recorded in that case was so weak to prevent a unambiguous assignment. We can estimate therefore the pK_a value of methane as a sort of limiting value to evaluate the basic potential of MgO and as the boundary between the reactivity of this oxide and that of CaO. The other three molecules reported in the table are less acidic than methane and do not react with MgO, but though on few particularly strong surface sites, they are dissociated by CaO.

4.2. Spectra of Adsorbed Superoxide. A detailed discussion on the structure of the various spectra of O₂⁻ on CaO is beyond the purposes of the present article. It has however to be noticed that a variety of superoxide species has been obtained as indicated by the heterogeneity of g_{zz} values in Figure 1, ranging between 2.104 and 2.089 (Table 2). One species only ($g_{zz} = 2.097$) was observed using hydrogen in experiments parallel to those discussed here.²⁴ Each of these values corresponds, in analogy with what observed on MgO, to a cation adsorption site with particular structural and coordinative features.²²

As the spectra in Figure 1 have been measured at 77 K, artifacts in the g_{zz} value determination due to "on site" dynamic effects can be excluded, as these effects take place at higher temperatures.

Surface bidimensional mobility after O₂⁻ generation cannot be, at variance, completely excluded: this means that the site of O₂⁻ stabilization could not coincide with the site where O₂⁻ has been generated because of spillover of the adsorbed species. In other words, the distribution of O₂⁻ species among various sites is not an artifact but is not, in the meantime, an indication of the site active in the R-H splitting.

Interestingly, the distribution of the superoxide ions on the various Ca²⁺ sites depends on the hydrocarbon involved in the experiment. In particular, Figure 1 shows that, whereas methane-oxygen coadsorption mainly generated superoxide species at high g_{zz} value (2.102), i.e., corresponding to Ca²⁺ sites with lower electrostatic potential, the interaction of the other hydrocarbons (with larger and less acidic molecules) leads to the formation of superoxide on sites at lower coordination and capable to exert a higher ionic field. It is not clear, at present, if the difference is due to the fact that different sites perform in the H⁺ abstraction from the various hydrocarbons or to the different steric hindrance of the molecules involved in the surface reaction. This topic is currently under investigation in our laboratory in particular as far as the role of the hydrocarbon pressure on the g_{zz} distribution is concerned.

4.3. Isotopic Exchange at the CaO Surface. The particular activity in the H/D isotopic exchange of the CaO surface hydroxyls (deuterioxylys) generated along the preparation of surface Fs(H)⁺ centers by irradiation was already observed and reported in a previous paper by some of us.²⁷ The phenomenon was observed contacting with D₂ or H₂ the surface containing Fs(H)⁺ or Fs(D)⁺ centers, respectively. The same phenomenon takes place (Figure 5b) with the centers generated via irradiation in hydrocarbon atmosphere. This fact is not surprising and in fact confirms that the nature of the F centers described in the present work (irradiation in hydrocarbon atmosphere) is essentially the same of those derived with the classic procedure of irradiation in H₂. The more intriguing fact is that the same OH (OD) group is active in the H/D substitution also when contacted with methane (Figur 5, parts c and d). This occurs according to the following equilibrium:



This reaction, or the reverse one



implies that at the CaO surface hydroxyl site the C-H (or C-D) bond cleavage occurs easily to allow the H/D substitution. At the present stage, the mechanism of this isotopic reaction is still obscure and is the object of further investigation.

5. Conclusions

Particular highly basic sites at the CaO surface are able to split heterolytically the C-H bond in alkanes of extremely low acidity (pK_a in the range between 48 and 51). This phenomenon has indirectly been monitored by EPR using as evidence of the C-H cleavage the formation of paramagnetic superoxide ions occurring via a SIET mechanism at the surface. Furthermore, when the surface containing the cleaved hydrocarbon fragments is irradiated, surface trapped electrons are formed by ionization of the organic anion. The spectra of Fs(H)⁺ centers exhibit a quite complex structure also because of the residual interaction of the unpaired electron with the hydrocarbon chain. Surface OH groups produced during the hydrocarbon splitting are active in the H/D isotopic substitution using either H₂ (D₂) or CH₄ (CD₄).

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