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EPR study of electron trapping on partially hydroxylated alkali-earth oxides occurring during SO₂ disproportionation.

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Abstract

We used the Electron Paramagnetic Resonance (EPR) technique to study the interaction of SO₂ molecules on bare and partially hydroxylated Alkali-Earth Oxides surface (AEOs). When SO₂ is adsorbed on the surfaces of higher basicity (CaO and SrO) disproportionation reaction occurs with formation of SO₂^{•-} radical. We show also that, when the same reaction is present on partially hydroxylated surfaces a fraction of the electrons exchanged during the redox process are trapped on the oxides surface forming colour centres ((H⁺)(e⁻) centres).

1. Introduction.

It is well established that surface hydroxyl groups play a crucial role in dictating the chemical and physical properties of oxide surfaces [1,2]. The photochemical properties of TiO₂, for example, are strictly related to the presence of surface hydroxyl groups [3]. Another peculiar effect is the capability of electron trapping observed on partially hydroxylated alkali-earth oxides (AEOs) and not observed on fully dehydroxylated surfaces.

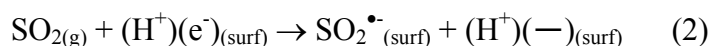
Surface electron trapping on oxides was first observed by Tench and Nelson in 1968 by exposing MgO to hydrogen and irradiating the material with UV light [4]. The phenomenon was tentatively attributed to the population of empty sites (anion vacancies) naturally present on the surface so

extending the well established De Boer model of bulk F centres. However, work performed in the past decade, and recently summarized in a review article, has shown the different nature of these centres [5]. Exposure of MgO to hydrogen atoms results in fact in the spontaneous ionization, at temperatures as low as 77 K, of H^\bullet , with the subsequent formation of excess electrons and extra protons on the surface. These centres have been labelled $(H^+)(e^-)$ to clearly indicate that they result from the ionization of the H^\bullet atom, with subsequent stabilization of the electron on low-coordinated cationic sites, and of the proton on a surface oxide anion to form an hydroxyl group which plays an essential role in the stabilization of the centre.

Surface excess electrons are highly reactive centres and their presence can lead to important changes in chemical (and catalytic) reactivity of the materials. For example, differently from bare MgO, an electron-rich MgO surface is able to activate rather inert molecules such as N_2 and CO with formation of the corresponding radical anions [6,7]. Both trapped electrons and surface radical anions were monitored by Electron Paramagnetic Resonance, a high sensitive spectroscopy and the reference technique for detection and characterization of radical intermediates [8,9].

In previous work from our laboratory the interaction of SO_2 molecules with the bare and the electron rich surface of MgO and CaO was investigated [10]. The interaction of sulphur containing molecules with basic oxides is of paramount importance in the field of pollutants abatement from automobile exhaust [11, 12] and has been the object of a relevant number of both experimental [13, 14] and theoretical [15, 16] investigations. In particular the high reactivity of the basic surface of alkali earth oxide is the peculiar factor to entail the reactions with sulphur dioxide which are not limited to the simple neutralization of the acidic molecule (sulphites formation) typical of the surface chemistry of some non metal oxide, but involve also complex disproportionations (e.g CO [7] on AEO). In the mentioned work from our group [10] two radical anions intermediate of the interaction of SO_2 with AEOs, namely $SO_2^{\bullet-}$ and $S_2O^{\bullet-}$, were identified by EPR whose abundance depends on the basicity of the oxide. The formation of $SO_2^{\bullet-}$ (the most abundant of the two radicals) occurs upon SO_2 absorption on the bare surface of the oxide and it is due to a

disproportionation reaction induced by oxide ions present, with low coordination (O^{2-}_{LC}), at the surface as shown in eq. 1. In the case of the electron rich surface, the basic reactivity does not vanish but is accompanied by the typical electron transfer reactivity associated to trapped electrons (Eq.2). Reaction 1 was observed on CaO only, because of the higher basicity of this oxide with respect to MgO.



In the same work [10] and in the case of CaO, an anomalous behavior of the spectral intensity of $(H^+)(e^-)$ centres has been observed and tentatively ascribed to a sort of regeneration mechanism of the centres themselves. In this paper the interaction of SO_2 with two basic oxides as CaO and SrO both in fully and partially dehydroxylated forms was studied in order to understand the effects of surface OH^- groups on SO_2 reactivity and to clarify the origin of electron trapping phenomena, caused by this reactivity at the surface of alkali-earth oxide.

2. Experimental.

SO_2 adsorption on CaO and SrO was studied on two distinct types (namely highly dehydroxylated and partially dehydroxylated) of material. In both cases the two oxides were prepared by slow decomposition of the corresponding carbonates under vacuum as described elsewhere [17]. Thermal activation at 1173 K produces virtually hydroxyl free samples, which have been investigated in previous studies [18,19]. Partially dehydroxylated materials were obtained by thermal decomposition of the same carbonates at 1023K for CaO and 1043K for SrO. At this temperature few OH^- groups are left on the surface at low coordinated sites [2,19].

$Ca(CO_3)$ 99.999% and $Sr(CO_3)$ 99.995% were purchased by Sigma Aldrich. High purity SO_2 was purchased by Aldrich and purified by the “freeze –thaw” method prior adsorption. In all experiments here reported SO_2 interaction with AEOs was always carried out contacting at room

temperature the surface with an increasing amount of gas according to the following steps: 1 mbar, 2 mbar, 5 mbar and 10 mbar and monitoring the radical evolution after each step and for several hours after the last one.

Double integration of the spectra was performed using the Win-EPR program. Traces of Mn^{2+} ions in the bulk of CaO are practically unavoidable and generate a weak EPR signal with the typical manganese sextet centred close to the free electron g value. A Mn^{2+} hyperfine line always appears in the EPR spectra of CaO (labelled with a star) and has been used as internal standard for g values evaluation.

3. Results.

After SO_2 absorption either on CaO or on SrO, two distinct types of paramagnetic signals appear, the first one due to sulphur containing species ($\text{SO}_2^{\bullet-}$) and the second one ascribed to electrons trapped at the surface of the oxides ($(\text{H}^+)(\text{e}^-)$ centres).

Figure 1 reports the EPR spectra obtained after SO_2 contact with both highly (Fig.1A) and partially (Fig.1B) dehydroxylated CaO surface. In the former case (surface activated at 1173K) only one type of signal is observed after SO_2 adsorption. The signal is due to the formation of $\text{SO}_2^{\bullet-}$ radical anions whose spectral intensity increases in parallel with the amount of adsorbed SO_2 . This species has been observed in the past in different systems and, in the case of AEOs, the existence of two slightly different species, differing in the g_{zz} parameter (Fig. 1) was reported [10,20]. The abundance of the two species ($\text{SO}_2^{\bullet-}$ radicals adsorbed on different surface sites) strictly depends pre-treatment. In the case of the partially dehydroxylated surface a new signal appears beside that of $\text{SO}_2^{\bullet-}$ whose intensity grows dose after dose (Fig. 1B). The second signal is characterized by a powder pattern dominated by an axial feature and was widely investigated in our laboratory in the past [5]. Such signal can be unambiguously assigned to the surface colour centres corresponding to trapped electrons at the oxide surface [21] ($(\text{H}^+)(\text{e}^-)$ centres).

The quantitative evolution of all paramagnetic species ($\text{SO}_2^{\bullet-}$ and $(\text{H}^+)(\text{e}^-)$ centres) observed on CaO in the two dehydration states have been obtained by double integration of the spectra and is reported in Fig. 2.

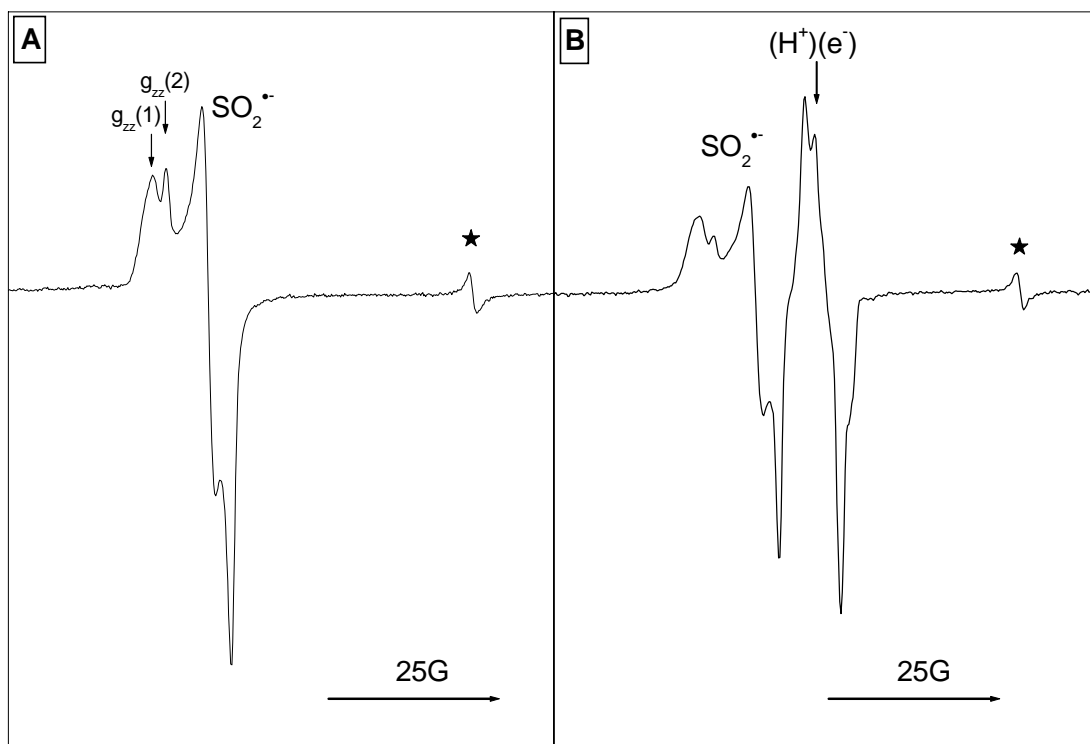


Figure 1: SO_2 adsorption on CaO. A) highly dehydroxylated surface. B) Partially dehydroxylated surface. In both cases spectra were obtained after absorption of 10 mbar SO_2 . A star indicates the Mn^{2+} impurity. The arrow indicate the g_{zz} factors of the slightly different $\text{SO}_2^{\bullet-}$ species. Spectra recorded at RT with modulation amplitude of 1G and 1mW of microwave power.

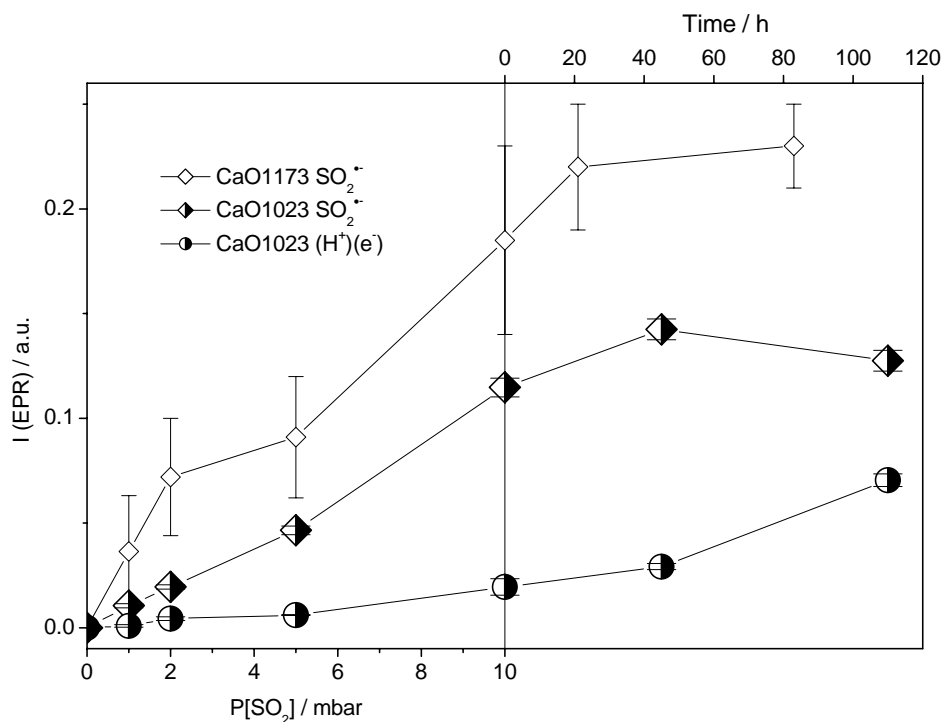


Figure 2: Paramagnetic centres intensity on CaO reported as a function of the dose pressure (left hand side) and of the time elapsed after the last dose (right hand side).

As to SrO surface, in figure 3 the EPR spectra, obtained upon SO₂ contact with highly (Fig.3A) and partially (Fig.3B) dehydroxylated materials, are reported. The reactivity is very similar to that observed for CaO. The SO₂•⁻ species only was, in fact, observed for the surface activated at 1173 K (Fig.3A) whereas in the case of the sample treated at 1043 K (Fig.3B) SO₂•⁻ is accompanied by a signal typical of (H⁺)(e⁻) centres on SrO [17]. The quantitative evolution of all paramagnetic species (SO₂•⁻ and (H⁺)(e⁻) centres) observed on SrO is reported in Fig.4.

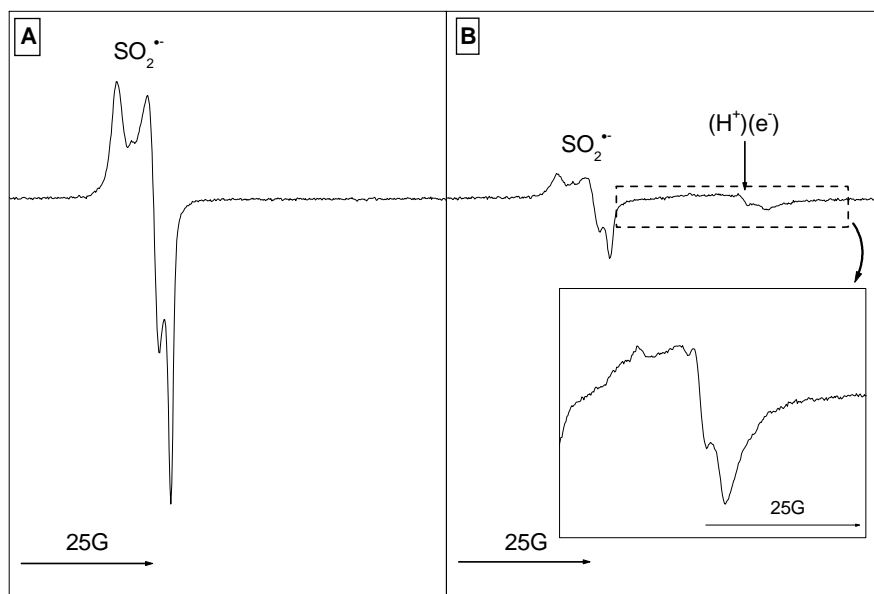


Figure 3: SO₂ adsorption on SrO. A) highly dehydroxylated surface. B) Partially dehydroxylated surface. Spectrum obtained after absorption of 5 mbar of SO₂. Inset in section B shows the magnification of (H[•])(e⁻) centres signal. Spectra recorded at RT with modulation amplitude of 1G and 1mW of microwave power.

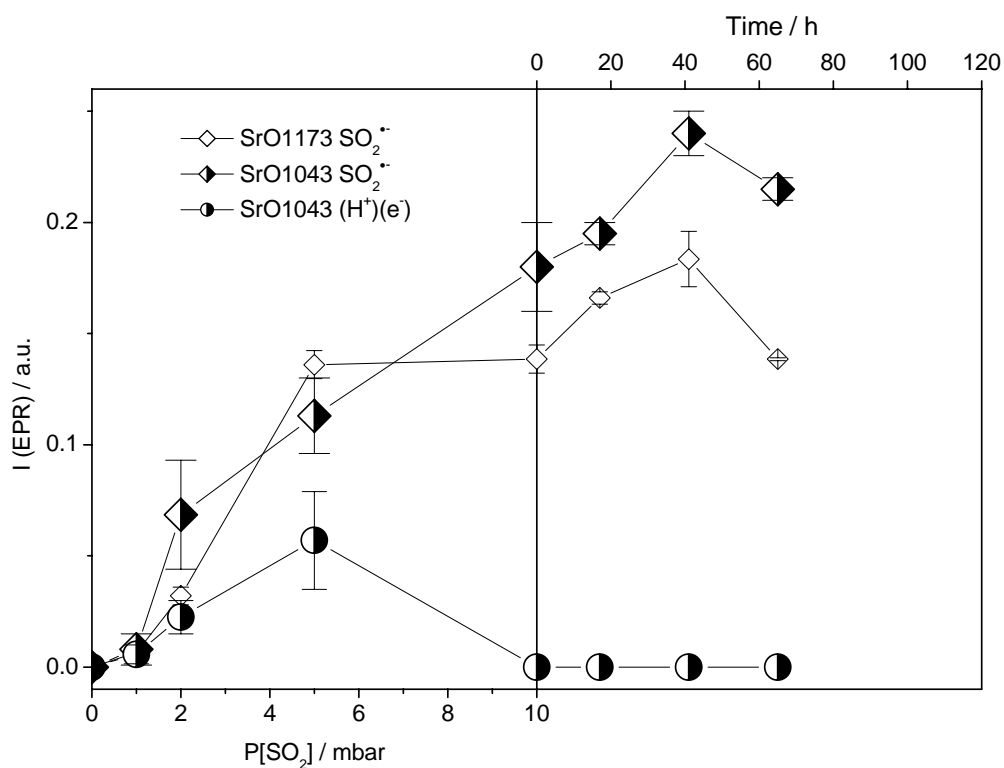


Figure 4: Paramagnetic centres intensity on SrO reported as a function of the dose pressure (left hand side) and of the time elapsed after last dose (right hand side).

4. Discussion

The SO₂ interaction with alkali earth oxides is rather complex and has been largely studied in the past with various techniques for its importance in heterogeneous catalysis. It is well established that various types of reaction channels exist for this interaction including those involving diamagnetic species. In particular SO₂ interaction with low coordinated surface oxygen (O_{LC}²⁻) leads to surface species as sulphites and sulphates groups [22,23].

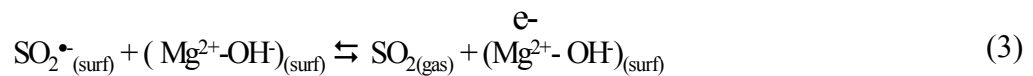
Figure 1 and 3 clearly show that two paramagnetic species can be formed at the surface of AEOs when exposed to SO₂. The first one is the SO₂^{•-} radical ion which is characterized by a quasi axial *g* tensor and has the structure expected for 19 electrons three-atomic radicals like O₃^{•-} or ClO₂^{•-} whose *g* tensor is only slightly affected by the surrounding crystal field [24]. For this reason the signal does not show any relevant difference between the two oxides surfaces. Formation of this radical on AEOs is reported in the literature [10,20], and in the case of bare oxides, is due to a surface disproportionation reaction induced by basic O_{LC}²⁻ sites as described by Equation 1 in Section 1. Moreover SO₂^{•-} formation, in all the cases here reported, proceeds after the last step of gas adsorption indicating the existence of some slow step in the SO₂ interaction with basic oxide surface.

The most interesting effect due to the interaction of SO₂ with the surface of CaO and SrO however is the formation of colour centres (H⁺)(e⁻) that occurs when the absorption is carried out on partially hydroxylated surface. This aspect is particularly evident in the case of CaO as the trapped electron signal is formed already in the early steps of SO₂ absorption and constantly increases with time (Fig. 2). A similar behaviour is observed in the case of SrO which is limited, however, to the first steps of SO₂ adsorption (Fig. 4). Double integration of the (H⁺)(e⁻) signal shows in fact that after a dose of 5mbar SO₂ the intensity of this signal is comparable to that observed on CaO but at variance with what observed on CaO, (H⁺)(e⁻) centres are completely bleached after a further SO₂ dose (Fig. 4).

The observed phenomena, and the different trend observed for the two oxides, can be rationalized as follows.

a) Sulphur dioxide undergoes disproportionation at the surface of basic oxides. This is likely a side reaction, the main phenomenon being the direct formation of surface sulphites which does not involve a change of the sulphur oxidation number. The reaction is illustrated by Equation 1: the radical anion $\text{SO}_2^{\bullet-}$ represents the reduced counterpart in the disproportionation that occurs at room temperature.

b) If residual hydroxyl groups are still present on the surface (less dehydrated materials) an OH group itself in cooperation with one (or more) low coordination cation [5] can act as an electron trap and compete with SO_2 molecules in scavenging the electron released along the disproportionation reaction. The process can be written according to the following equilibrium.

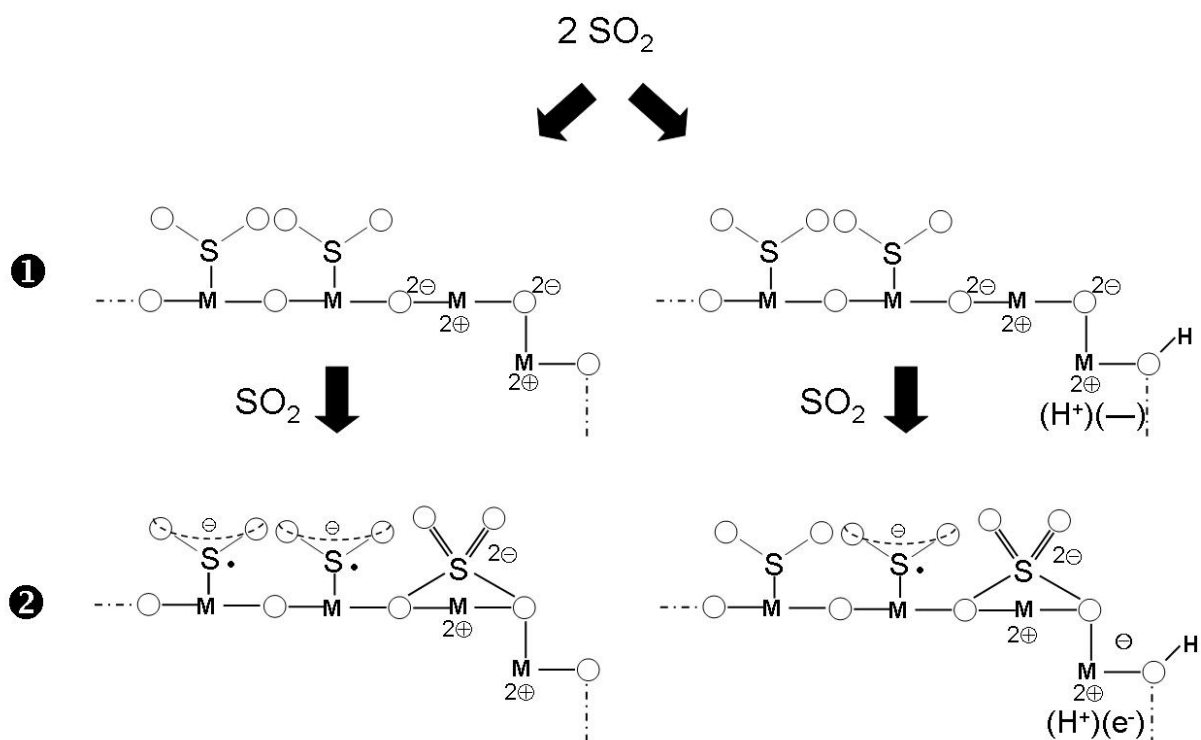


The last term in Eq. 3 is the colour centre indicated as $(\text{H}^+)(\text{e}^-)$ in the text. The symbol adopted in the equation outlines the role of a pre-existing surface OH group in generating a trap site.

c) The stability of the two reduced centres ($\text{SO}_2^{\bullet-}$ and $(\text{H}^+)(\text{e}^-)$) is not the same for the two oxides. In the case of CaO the stability of the two centres is probably comparable. Both are formed since the beginning of the reaction and, though $\text{SO}_2^{\bullet-}$ is present in higher amount, for prolonged exposition to SO_2 a progressive decrease of $\text{SO}_2^{\bullet-}$ concentration, accompanied by an increase of that of colour centres, is observed (right hand side of Fig.2) The opposite occurs in the case of SrO. The initially formed $(\text{H}^+)(\text{e}^-)$ are progressively consumed (Fig. 4) indicating that, in this case, the equilibrium in Eq. 3 is displaced toward the left hand side. This different stabilization energies of an electron in the two analogous surface traps available on CaO and SrO, is probably the reason of the observed behaviour. The electric field exerted by cations on the electron is in fact, crucial for the

formation of surface colour centres [25]. Sr^{2+} ions are certainly less efficient in electron trapping than smaller Ca^{2+} ones.

In conclusion we have monitored the disproportionation of SO_2 at the surface of fully dehydrated and partially hydrated CaO and SrO . Surprisingly the reduced term of the reaction performed at room temperature on partially hydroxylated materials can be either a $\text{SO}_2^{\bullet-}$ radical anion or a surface trapped electron. While on SrO the trapped electrons act just as intermediates and are eventually consumed leaving only $\text{SO}_2^{\bullet-}$ as reduced product, on CaO the two centres have comparable stability and are simultaneously present at the surface along the reaction. Scheme 1 illustrates the whole reaction pathways described in this paper.



Scheme 1: SO_2 reaction on bare surface (left hand side) and on the partially hydrogenated surface (right hand side).

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