



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

Stefano Livraghi, Maria Cristina Paganini*, Elio Giamello

Dipartimento di Chimica IFM, Università di Torino and NIS, Nanostructured Interfaces and Surfaces, Centre of Excellence, Via P. Giuria 7, I-10125 Torino, Italy

ARTICLE INFO

Article history:

Received 26 April 2011

Received in revised form 26 July 2011

Accepted 15 August 2011

Available online 7 September 2011

Keywords:

SO₂

EPR

Alkali-earth oxides

Surface

Catalysis

Disproportionation

ABSTRACT

We used the Electron Paramagnetic Resonance (EPR) technique to study the interaction of SO₂ molecules on bare and partially hydroxylated alkali-earth oxide (AEO) surface. When SO₂ is adsorbed on the surfaces of higher basicity (CaO and SrO) disproportionation reaction occurs with the 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 oxide surface forming colour centres ((H⁺)(e⁻) centres).

© 2011 Elsevier B.V. All rights reserved.

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 TiO₂ photochemical properties, 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 for 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]. MgO exposure to hydrogen atoms results in fact in the spontaneous ionization, at temperatures as low as 77 K, of H[•], 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[•] atom, with subsequent stabilization of the electron on low-coordinated cationic sites, and of the proton on a surface

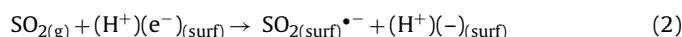
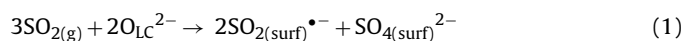
oxide anion to form hydroxyl group which plays an essential role in the stabilization of the centre.

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 N₂ 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 SO₂ 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 (sulphite formation) typical of the surface chemistry of some nonmetal 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 SO₂ with AEOs, namely SO₂^{•-} and S₂O^{•-}, were identified by EPR whose abundance depends on the oxide basicity. The formation of SO₂^{•-} (the most abundant of the two radicals) occurs upon SO₂ absorption on the bare surface of

* Corresponding author. Tel.: +39 011 6707576; fax: +39 011 6707855.
E-mail address: mariacristina.paganini@unito.it (M.C. Paganini).

the oxide and it is due to a disproportionation reaction induced by oxide ions present, with low coordination (O_{LC}^{2-}), 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 behaviour 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 materials. 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 1023 K for CaO and 1043 K 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 value 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 ($SO_2^{\bullet-}$) and the second one ascribed to electrons trapped at the surface of the oxides ($(H^+)(e^-)$ centres).

Fig. 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 1173 K) only one signal type is observed after SO_2 adsorption. The signal is due to the formation of $SO_2^{\bullet-}$ radical anions whose spectral intensity increases in parallel with the amount of adsorbed SO_2 . This species has been observed in the past in several 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 ($SO_2^{\bullet-}$ radicals adsorbed on different surface sites) strictly depends on the pre-treatment. In the case of the partially dehydroxylated surface a new signal appears beside that of $SO_2^{\bullet-}$ 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] ($(H^+)(e^-)$ centres).

The quantitative evolution of all paramagnetic species ($SO_2^{\bullet-}$ and $(H^+)(e^-)$ centres) observed on CaO in the two dehydration states has been obtained by double integration of the spectra and is reported in Fig. 2.

As to SrO surface, in Fig. 3 the EPR spectra, obtained upon SO_2 contact with highly (Fig. 3A) and partially (Fig. 3B) dehydroxylated materials, are reported. The reactivity is very similar to that observed for CaO. The $SO_2^{\bullet-}$ 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) $SO_2^{\bullet-}$ is accompanied by the typical signal of $(H^+)(e^-)$ centres on SrO [17]. The quantitative evolution of all paramagnetic species ($SO_2^{\bullet-}$ and $(H^+)(e^-)$ centres) observed on SrO is reported in Fig. 4.

4. Discussion

The SO_2 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 SO_2 interaction with low coordinated surface oxygen (O_{LC}^{2-}) leads to surface species as sulphite and sulphate groups [22,23].

Figs. 1 and 3 clearly show that two paramagnetic species can be formed at the surface of AEOs when exposed to SO_2 . The first one is the $SO_2^{\bullet-}$ radical ion which is characterized by a quasi axial g tensor and shows the structure expected for 19 electrons three-atomic radicals like $O_3^{\bullet-}$ or $ClO_2^{\bullet-}$ whose g tensor is only slightly affected by the surrounding crystal field [24]. For this reason the signal does not exhibit any relevant difference between the two oxide 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 Eq. (1) in Section 1. Moreover $SO_2^{\bullet-}$ formation, in all the cases here reported, proceeds after the last step of gas adsorption indicating the existence of some slow step in the SO_2 interaction with basic oxide surface.

The most interesting effect due to the SO_2 interaction with CaO and SrO surface 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 SO_2 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 step of SO_2 adsorption (Fig. 4). Double integration of the $(H^+)(e^-)$ signal shows in fact that after a dose of 5 mbar SO_2 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 SO_2 dose (Fig. 4).

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

- 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 Eq. (1): the radical anion $SO_2^{\bullet-}$ represents the

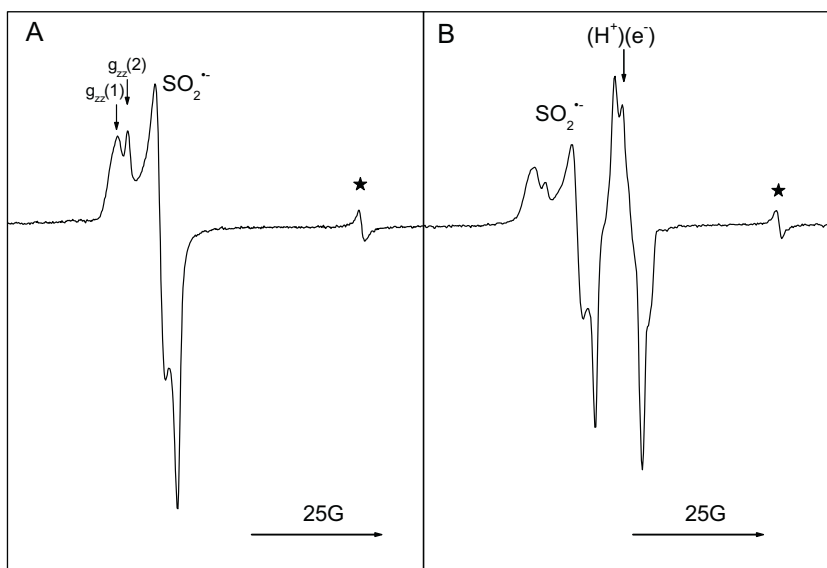


Fig. 1. SO_2 adsorption on CaO. (A) Highly dehydroxylated surface and (B) partially dehydroxylated surface. In both cases spectra were obtained after absorption of 10 mbar SO_2 . A star indicates the Mn^{2+} impurity. The arrow indicates the g_{zz} factors of the slightly different $\text{SO}_2^{\bullet-}$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

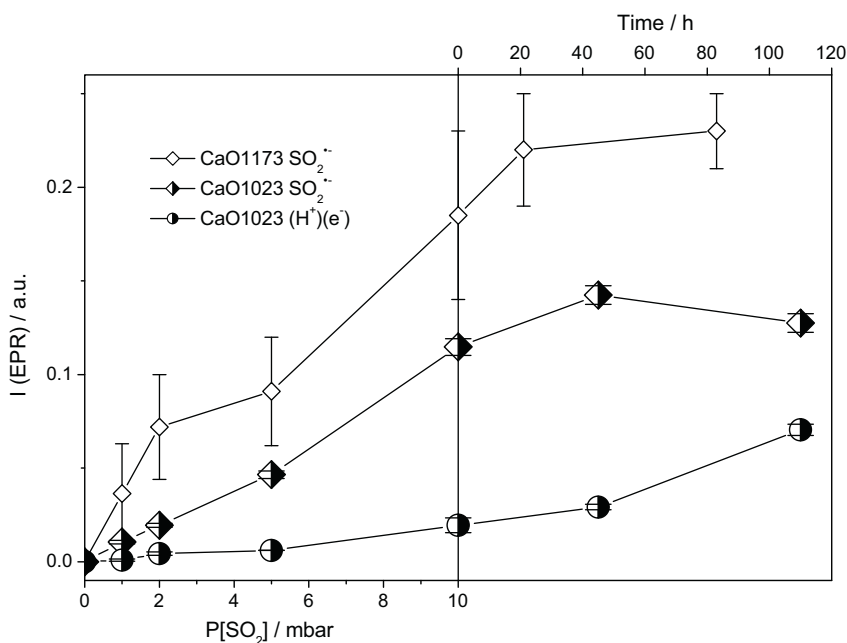
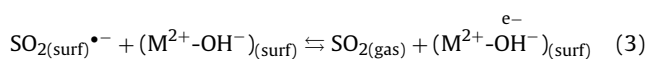


Fig. 2. Paramagnetic centre intensity on CaO reported as a function of the dose pressure (left hand side) and of the time elapsed after the last dose (right hand side).

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 towards the left hand side.

The presence of surface defects on AEOs has been extensively studied in the past from our group [2,5,25], and it has been demonstrated that defect sites due to non-regular morphology,

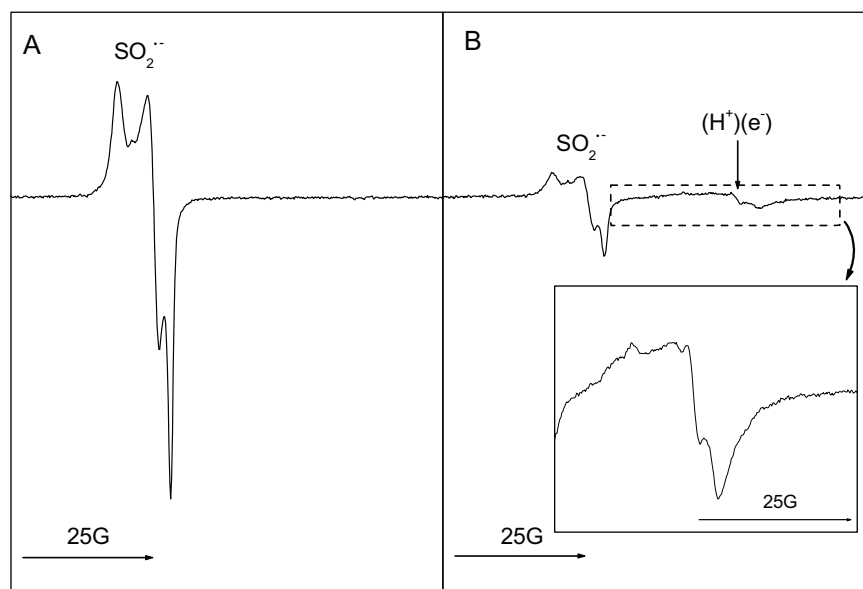


Fig. 3. SO_2 adsorption on SrO. (A) Highly dehydroxylated surface and (B) partially dehydroxylated surface. Spectrum obtained after absorption of 5 mbar of SO_2 . Inset in section B shows the magnification of $(\text{H}^+)(\text{e}^-)$ centres signal. Spectra recorded at RT with modulation amplitude of 1 G and 1 mW of microwave power.

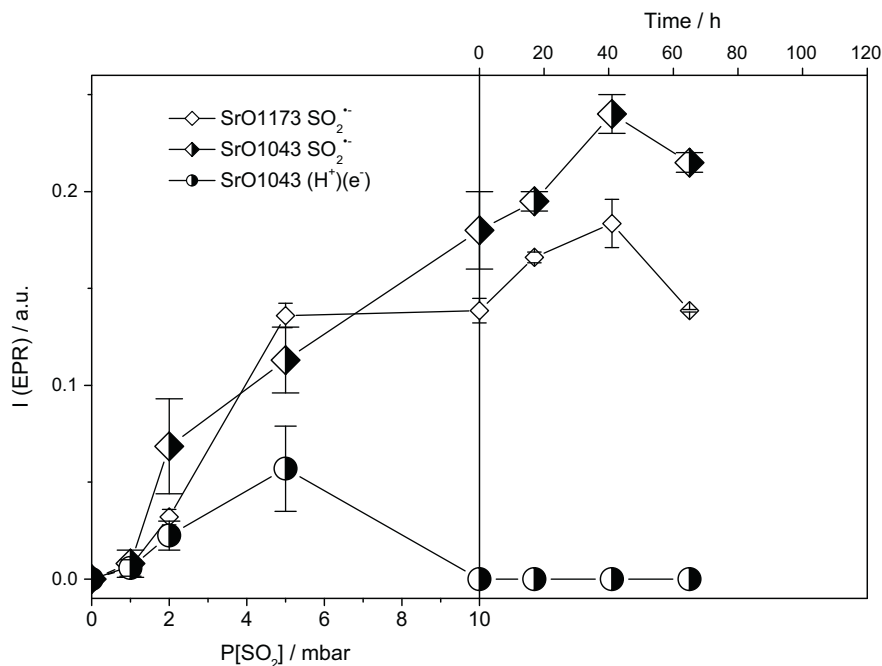
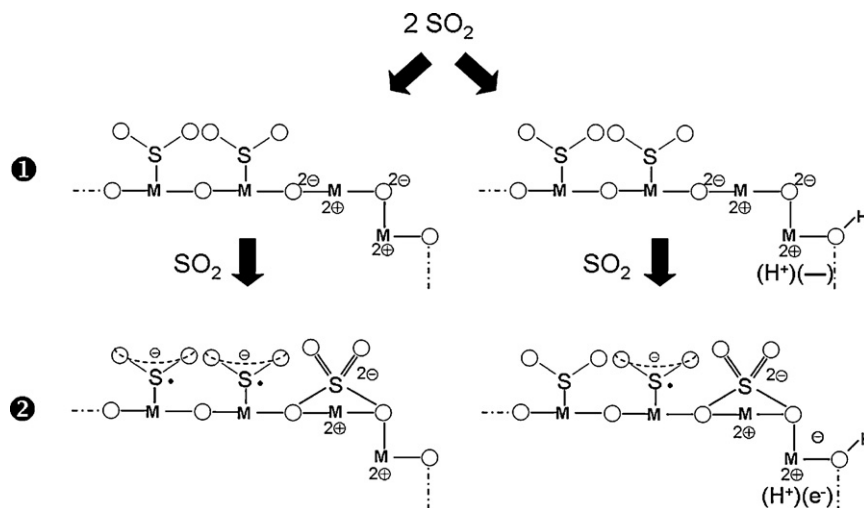


Fig. 4. Paramagnetic centre intensity on SrO reported as a function of the dose pressure (left hand side) and of the time elapsed after last dose (right hand side).

that generates kinks, steps and reverse corner sites, in general low coordinated sites, are present on both oxides. The reactivity of these sites has been proved by sorption of probe molecules able to measure the surface basicity and acidity of these sites. The surface sites responsible for electron stabilization include a 3C corner mono-vacancy, a 4C mono-vacancy and anion-cation divacancy. It has to be considered also that the surface coverage of OH groups depends on different temperature used in thermal activation, and that colour centres are strictly correlated to these species. In fact as reported in previous paper [5] it has been demonstrated that electrons are trapped in shallow traps close to OH sites still present on the surface. After thermal activation the residual OH groups are preferentially localized on the low coordinated surface sites (3 and 4 coordinated sites) [19]. According to this evidence

process described in Eq. (3) concerns only these low coordinated sites.

Generally regardless of the AEOs used, a common degree of morphological similarities exists on each oxide [26]. The observed different behaviour, between the two oxides, towards high SO_2 pressure is probably due to the different surface reactivities of the two oxides. SrO surface is more basic and in general more reactive towards adsorbed molecules and also promotes faster reaction of trapped electrons. It has been demonstrated several years ago by Tanabe et al. [27] and theoretically rationalized by Pacchioni et al. [28] that there is a strong correlation between the base strength and the cation dimensions and their position in the group, following the order $\text{MgO} < \text{CaO} < \text{SrO} < \text{BaO}$ and considering the Madelung potential across the series. The different behaviour along the series is due



Scheme 1. SO₂ reaction on bare surface (left hand side) and on the partially hydrogenated surface (right hand side).

to the linear increase in the lattice parameter from MgO to BaO. This results in a corresponding decrease of the Madelung potential, which for the heavier oxides, becomes less effective in stabilizing the lattice O²⁻ anions leading to enhanced charge donativity. Moreover the electric field exerted by cations on the electron is crucial for the formation of surface colour centres [2]. Sr²⁺ ions are certainly less efficient in electron trapping than smaller Ca²⁺ ones.

In conclusion we have monitored the disproportionation of SO₂ 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 SO₂^{•-} radical anion or a surface trapped electron. While on SrO the trapped electrons act just as intermediates and are eventually consumed leaving only SO₂^{•-} 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.

References

- [1] S.A. Chambers, T. Droubay, D.R. Jennison, T.R. Mattson, *Science* 297 (2002) 827–831.
- [2] F. Napoli, M. Chiesa, E. Giamello, E. Finazzi, C. Di Valentin, G. Pacchioni, *J. Am. Chem. Soc.* 129 (2007) 10575–10581.
- [3] U. Diebold, *Surf. Sci. Rep.* 48 (2003) 53–229.
- [4] A.J. Tench, R.L. Nelson, *J. Colloid Interface Sci.* 26 (1968) 364–373.
- [5] M. Chiesa, M.C. Paganini, E. Giamello, D.M. Murphy, C. Di Valentin, G. Pacchioni, *Acc. Chem. Res.* 39 (2006) 861–867.
- [6] M. Chiesa, E. Giamello, D. Murphy, G. Pacchioni, M.C. Paganini, R. Soave, Z. Sojka, *J. Phys. Chem. B* 105 (2001) 497–505.
- [7] E. Giamello, D. Murphy, L. Marchese, G. Martra, A. Zecchina, *J. Chem. Soc. Farad. Trans.* 89 (1993) 3715–3722.
- [8] S. Livraghi, M.C. Paganini, M. Chiesa, E. Giamello, *Res. Chem. Intermediat.* 32 (2006) 777–786.
- [9] M. Chiesa, E. Giamello, M. Che, *Chem. Rev.* 110 (2010) 1320–1347.
- [10] S. Livraghi, M.C. Paganini, E. Giamello, *J. Mol. Catal. A: Chem.* 322 (2010) 39–44.
- [11] J.A. Rodriguez, T. Jirsak, A. Freitag, J.Z. Larese, A. Maiti, *J. Phys. Chem. B* 104 (2000) 7439–7448.
- [12] Z. Xingying, Z. Guoshun, C. Jianmin, W. Ying, W. Xiao, A. Zhisheng, Z. Peng, *J. Phys. Chem. B* 110 (2006) 12588–12596.
- [13] P. Broqvist, H. Gronbeck, E. Fridell, I. Panas, *Catal. Today* 96 (2004) 71–78.
- [14] H. Gronbeck, *Top. Catal.* 28 (2004) 59–69.
- [15] A. Snis, I. Panas, D. Strömberg, *Surf. Sci.* 310 (1994) L579–L582.
- [16] W.F. Schneider, *J. Phys. Chem. B* 108 (2004) 273–282.
- [17] I. Purnell, M. Chiesa, R.D. Farley, D.M. Murphy, C.C. Rowlands, M.C. Paganini, E. Giamello, *Magn. Reson. Chem.* 40 (2002) 381–386.
- [18] C. Chizallet, G. Costentin, M. Che, F. Delbecq, P. Sautet, *J. Am. Chem. Soc.* 129 (2007) 6442–6452.
- [19] S. Coluccia, S. Lavagnino, L. Marchese, *Mater. Chem. Phys.* 18 (1988) 455–464.
- [20] R.A. Schoonheydt, J.H. Lunsford, *J. Phys. Chem.* 76 (1972) 323–328.
- [21] D. Ricci, C. Di Valentin, G. Pacchioni, P.V. Sushko, A.L. Shluger, E. Giamello, *J. Am. Chem. Soc.* 125 (2003) 738–747.
- [22] T. Kaljuvee, A. Trikkel, R. Kuusik, V. Bender, *J. Therm. Anal. Calorim.* 80 (2005) 591–597.
- [23] A.L. Goodman, P. Li, C.R. Usher, V.H. Grassian, *J. Phys. Chem. A* 105 (2001) 6109–6120.
- [24] M.J. Lin, J.H. Lunsford, *J. Phys. Chem.* 80 (1976) 635–639.
- [25] M. Chiesa, F. Napoli, E. Giamello, *J. Phys. Chem. C* 111 (2007) 5481–5485.
- [26] I.J. Purnell, M. Chiesa, R.D. Farley, D.M. Murphy, C.C. Rowlands, M.C. Paganini, E. Giamello, *Magn. Reson. Chem.* 40 (2002) 381–386.
- [27] K. Tanabe, Y. Fukuda, *React. Kinet. Catal. Lett.* 1 (1974) 21–26; M. Mohri, K. Tanabe, *J. Catal.* 44 (1976) 50–56.
- [28] G. Pacchioni, J.M. Ricart, F. Illas, *J. Am. Chem. Soc.* 116 (1994) 10152–10158.