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COMMUNICATION

On the simple complexity of CO on oxide surfaces: facet-specific donation and backdonation effects revealed on TiO₂ anatase nanoparticles

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Abstract: Atomic-scale relationships between structure of TiO_2 surfaces and physical-chemical properties of surface sites, functional for titania–based applications, can be obtained from IR spectroscopy using carbon monoxide (CO) as molecular probe. In the literature, it is reported that strongly unsaturated cationic Ti sites (Lewis acid), important for reactivity, should cause a higher upshift of the CO stretching frequency. By IR-spectra of CO on TiO_2 nanomaterials and theoretical analyses, here we challenge this model. We show that the stretching frequency of adsorbed CO results from synergic and facet-dependent CO-surface donation (upshift)/surface-CO backdonation (downshift). Our results imply that the interaction of adsorbed molecules with the Ti centers is tuned by the surface oxygen atoms of the first coordination sphere, which play an active role as indirect electron density donors (Lewis base).

Titania (TiO_2) is among the most studied semiconductors due to its importance for sustainable processes with applications in the energy/power, healthcare/medical, engineering and consumer goods domains.[1] These processes take place at the surfaces of TiO_2 nanostructured films or nanoparticles and involve a multiplicity of chemical events dictated not only by the nature, concentration and spatial (de)localization of defects, but also, at a deeper level, by the type and heterogeneity of the exposed surfaces.[1] Whereas surface structures down to monoatomic-height step edges can be investigated by microscopies like STM in single-crystal TiO_2 materials,[2,3] fine surface details still remain elusive in nanoparticles. This is the domain of molecular probes: species whose spectroscopic behavior is shaped by the nature, the local structure and the electronic states of the adsorbing sites. By harnessing this sensitivity, IR experiments might catch a fleeting glimpse of surface chemistry; for example, the extent of bond weakening deduced for the probe from IR data is normally correlated with the ability of the surface sites to perturb electronic states and ignite activation of the adsorbates.[4] As recognized from the first seminal findings[5] to recent advances,[6] carbon monoxide (CO) is among the most informative probes, owing to the high sensitivity of its internal stretching mode frequency (νCO) to interactions with the surface

sites. This is due to its quite unique electronic structure, shown in Figure 1, which enables CO to act simultaneously as donor and acceptor of electron density. On this basis, CO-surface site interactions have been traditionally classified in three types: (i) electrostatic interactions, (ii) electron density donation from the highest occupied molecular orbital (HOMO) of CO, 5σ, and (iii) backdonation of electron density from the metallic center to the lowest unoccupied molecular orbitals (LUMO) of CO, $2\pi^*$.[7,8a-b] Even on regular surfaces, these mechanisms are simultaneously active, deeply interlaced with each other and difficult to disentangle from the interactions among adsorbed molecules. Nevertheless, a general agreement settled down on the massive predominance of mechanisms i) and ii) over mechanism iii)[9] in the absorption of CO on alkali and alkaline-earth oxides. This predominance was also highlighted for Ti^{4+} sites in (110) rutile-TiO_2,[8c, 10] and, very recently, even in stoichiometric and non-stoichiometric (101) surfaces of anatase-TiO_2.[6b] As a result, CO is generally regarded as the system-of-choice for probing both the relative polarizing power/Lewis acidity and the structure of cationic surface sites: the higher the wavenumber of adsorbed CO, the higher the coordinative unsaturation of the site.[11]
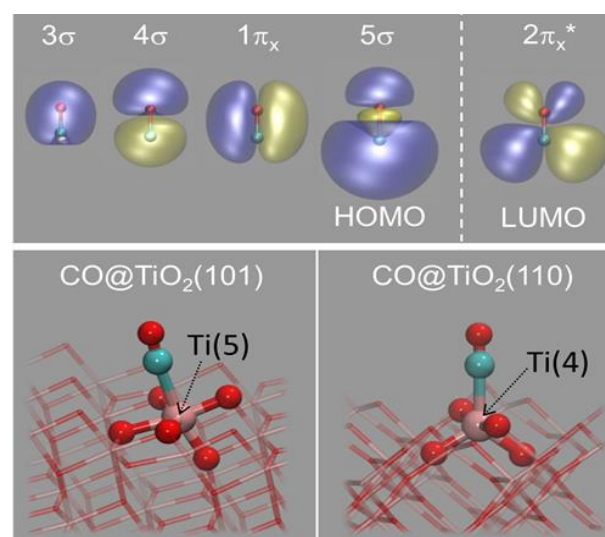

Figure 1. Top: the electronic structure of CO. From left to right, with increasing energy: the occupied orbitals 3σ, 4σ, $1\pi_x$, and 5σ (HOMO), and the $2\pi_x^*$ LUMO. Only the x-orbital of the 1π and $2\pi^*$ pairs of degenerate states is shown. Positive lobes: blue, negative: yellow. Bottom: optimized structures for the adsorption of CO on: a Ti(5) site of the anatase (101) surface; a Ti(4) site of the anatase (110) surface. CO, the Ti site, and its coordination environment are shown in ball-and-sticks. Atom colors: C=cyan; O=red; Ti=pink.

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       Supporting information (SI) for this article is given via a link at the
       end of the document.

This criterion is based on a sound reasoning: a higher unsaturation implies a stronger polarizing power and/or Lewis acidity of the site, and, in the second case, a greater withdrawal

of electron density from the probe. As the CO HOMO has antibonding character (see Figure 1, top), interaction with surface cations should cause a strengthening of the C-O bond, experimentally detectable by an upshift of the CO stretching band. By induction, this argument, originally put forward for insulating materials (e.g. MgO,[12,13] Al_2O_3[14]), has been transferred to semiconductor oxides involving group 4 transition metals,[15] TiO_2 included, and the concept that higher νCO wavenumbers are associated to strongly unsaturated and generally more reactive Ti centers, for example tetracoordinated (Ti(4)) rather than pentacoordinated (Ti(5)) sites, has sedimented throughout the years.[6,9,11,16,17] Herein, we show that exactly the opposite occurs at the (101) and (110) surfaces of anatase and we draw attention to a too-often overlooked character of TiO_2 materials: oxygen atoms.[18]
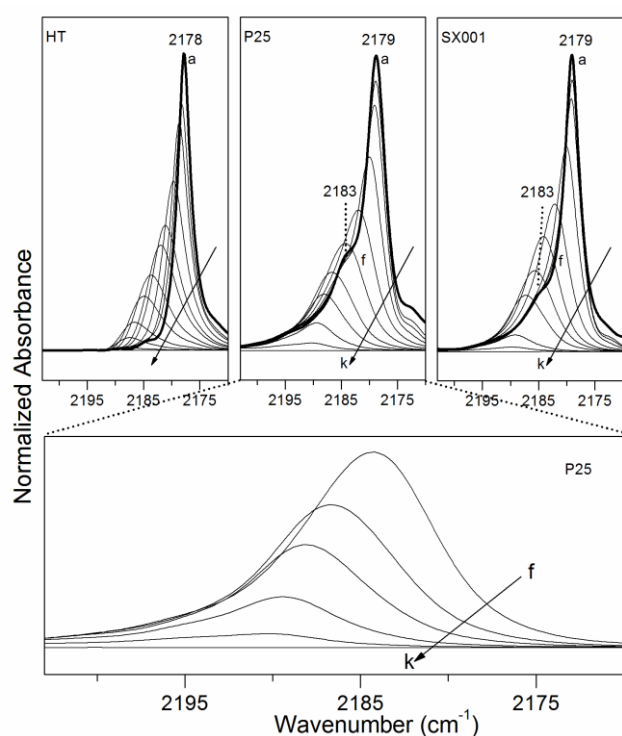

Figure 2. IR spectra of CO adsorbed at 100 K (decreasing coverage in the sense of lettering) on HT (left), P25 (center) and SX001 (right) outgassed at 873 K. Bottom panel: zoomed view of IR spectra at low CO coverage on P25

To determine the νCO values associated to Ti(5) and Ti(4) sites, we performed IR experiments on three types of fully-oxidized anatase TiO_2 nanoparticles (see Supporting Information (SI), Figures S1-S4) containing different relative proportions of (101) and (110) facets, which expose Ti(5) and Ti(4) sites respectively (Figure 1 and Figure S5). A first obstacle are adsorbate-adsorbate interactions, both dynamic and static in nature, which introduce additional factors affecting the frequency of adsorbed CO molecules.[9,19] Dynamic lateral interactions are due to the coupling between the vibrating dipoles of the adsorbed molecules, and result in an upshift of νCO with respect to the singletone. On the other hand, static interactions contain direct

(due to the electrostatic interactions of the static dipoles) and indirect (interaction via the surface) contributions, both resulting in a decrease of νCO with respect to the singletone. For CO adsorbed on oxides, static interactions prevail by far on the dynamic ones, and then a νCO downshift occurs when increasing the CO coverage.[19] Adsorbate-adsorbate interactions depend on the distance among adsorbing sites, and in our case they should be weaker (and the downshift smaller) at (110) facets compared to (101) ones because of the longer distance between Ti-sites (5.46 vs. 3.80 Å respectively). To avoid any of these additional contributions to νCO, we decreased the CO content of each sample from full coverage (θ=1) to the low coverage regime ($\theta \rightarrow 0$), where the CO-site interactions are largely prevailing over the CO-CO ones. The first sample, HT, consists of anatase TiO_2 nanoparticles with a well-defined truncated bipyramid shape, mainly limited by flat (101) surfaces exposing Ti(5) centers.[20] Accordingly, the IR spectrum for θ=1 shows only one sharp band at 2178 cm^{-1} (Figure 2, left, curve a), which gradually shifts to 2188 cm^{-1} with a progressive broadening when the coverage is decreased (curve a to k), owing to the decrease of CO-CO interactions.

Turning to TiO_2 P25, the anatase/rutile mixture (ca 80/20 by weight) considered as a benchmark for relevant heterogeneous photocatalytic processes, the spectrum at high CO coverage (Figure 2, center panel, curve a) exhibits a main peak at 2179 cm^{-1}, due to CO on anatase (101) facets, and a partially resolved shoulder at 2183 cm^{-1}, due to CO on anatase (110) facets.[20] The same occurred for CO on SX001 (by Solaronix), a pure TiO_2 anatase powder (see SI) (Figure 2, right panel, curve a). The strong similarity between data obtained for P25 and SX001 confirms that the νCO bands observed for P25 in this range are due only to CO adsorbed on the main anatase fraction of this material. By decreasing the CO coverage, the peak at 2179 cm^{-1} follows the same evolution observed for HT, while the component at 2183 cm^{-1} is nearly stable at the early steps of desorption (curves a-c), then gradually shifts to higher frequencies. Therefore, the signal due to CO on (110) facets, which is less affected by the decrease of the CO-CO interactions, is upshifted to a lower extent compared to the main peak. Interestingly, this trend continues by further decreasing the CO coverage and the signals overlap with each other (bottom panel). Because results obtained for TiO_2 HT provide evidence of CO left adsorbed on TiO_2 (101) facets in this low CO pressure regime, this behavior suggests that in the absence of adsorbate-adsorbate interactions CO on (101) and (110) facets seem to exhibit similar internal stretching frequencies. These results are difficult to accommodate into the accepted frame, which predicts that a higher unsaturation [Ti(4) on (110) vs. Ti(5) on (101)] should produce a higher νCO-upshift.[11]

To rationalize these findings, we modeled CO adsorption on regular (101) and (110) anatase surfaces at the $\theta \rightarrow 0$ limit by DFT calculations on periodic slab models, an approach already successful for the θ=1 regime[20,21] (see SI, section 2.1). Two different adsorption geometries were found: whereas CO at the (101) surface saturates a Ti(5) center in a pseudo-octahedral environment, CO is bound to a Ti(4) site of the (110) surface in a trigonal-bypiramid geometry, with the C atom on the bypiramid basis and the CO axis nearly perpendicular to the surface (Figure 1, bottom).

Table 1. Distances, binding energies BE and CO frequency ν_{CO}.

	Ti_c[a]	BE (kJ mol⁻¹)	Ti-C (Å)	C-O (Å)	νCO[b] (cm⁻¹)	Ti-O[c] (Å)	C-O$_S$[d] (Å)
(101)	5	38.5	2.345	1.129	2196.2	1.854	2.835
						1.871	2.856
						1.975	2.856
						1.975	3.024
						2.013	
(110)	4	50.2	2.249	1.130	2187.6	1.830	2.646
						1.830	2.777
						1.885	
						1.892	

[a] Coordination of the Ti center. [b] scaled values (f=1.011754, see SI). [c] Coordination distances of the Ti site. [d] O$_S$: surface oxygens closest to C.
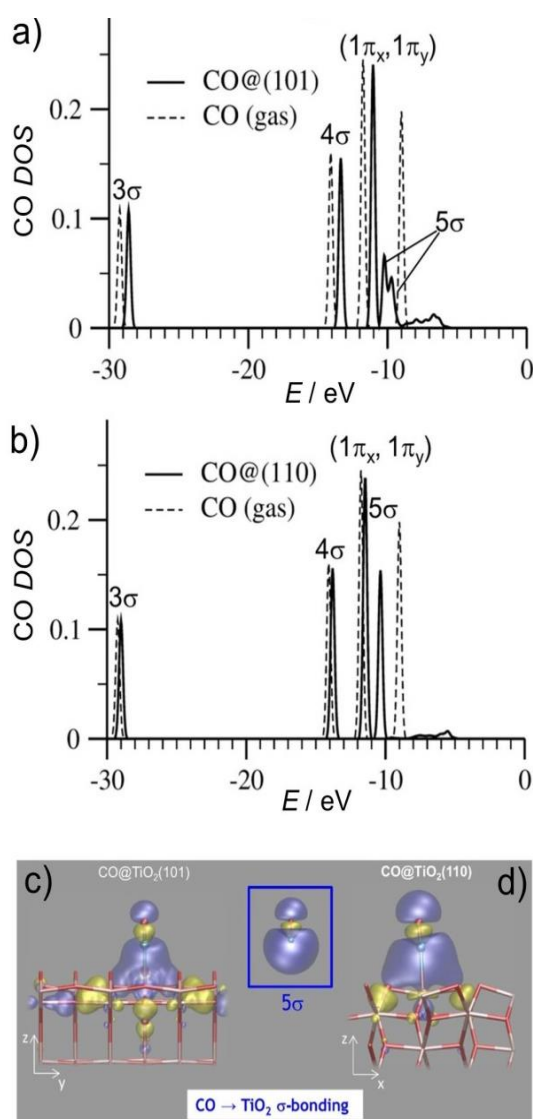

Figure 3. CO DOS for a) CO@TiO₂(101) and b) CO@TiO₂(110) (the DOS of gas-phase CO is also shown). The orbitals of c) CO@TiO₂(101) and d) CO@TiO₂(110) representing σ-bonding from the 5σ state of CO (central inset) to the surface. Further data on the electronic structure analysis are in SI, Section 2.2. Positive lobes: blue, negative: yellow. Atom colors as in Figure 1.

The data in Table 1 show that the binding energy is greater, the Ti-C distance is shorter and the separation of the C atom from the closest surface oxygens is also much shorter for CO at the Ti(4) sites of TiO₂(110). Hence, the Ti(4) sites interact more strongly than the Ti(5) ones with CO; this suggests a stronger Lewis acidity which, according to the generally accepted model, should be accompanied by a higher CO stretching frequency.[6h,11,17] Instead, in keeping with the trend outlined experimentally, at the θ→0 limit we obtain for Ti(4) a νCO value lower than for Ti(5), and even a slightly longer C-O bond distance.

To shed more light, we inspect the electronic structure of the two systems. The density of states projected on the C-O atoms (CO DOS, Figure 3a,b) shows a major stabilization of the CO HOMO upon adsorption. At the (101) surface, the 5σ is split in two main peaks, indicating the mixing of the CO HOMO with the TiO₂(101) states and a delocalized CO-surface σ-bonding (Figure 3c). Conversely, for CO at the (110) surface, the sharp 5σ peak and its greater stabilization compared to TiO₂(101) evidence a localized interaction with the Ti(4) site, depicted in Figure 3d, and a stronger σ-donation to the empty d states of Ti, as confirmed by the more pronounced electron density accumulation at the Ti-C bond (Figure 4d). Therefore, binding of CO to Ti(4) causes, compared to Ti(5), a greater depopulation of the CO HOMO, a stronger Ti-C bond, and a lower CO stretching frequency, which still remains unexplained.
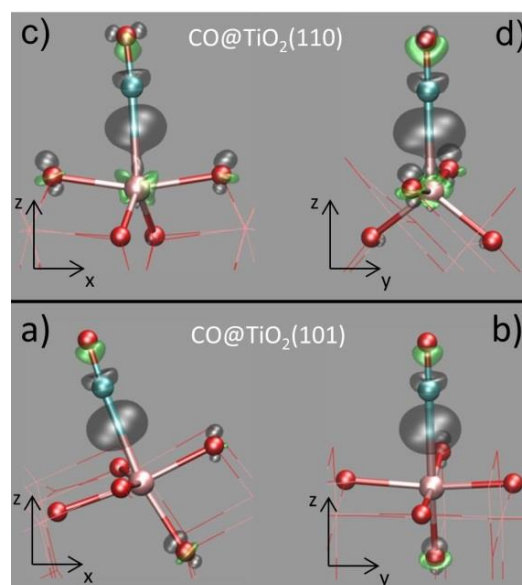

Figure 4. Bonding charge density Δρ on the xz (left) and yz (right) planes. Charge accumulation regions = grey, depletion regions= green. Δρ (see e.g. Refs. 8a and 22, and paragraph 2.2.2 in the SI) is the change in electronic charge upon bringing CO to the surface. (See also contour plots, SI, Figure S15). Results were validated with the hybrid functional PBE0 (SI, Figure S16).

But figure 4 also reveals that, upon adsorption at the Ti(4) site of TiO₂(110), the electron density of CO increases on top of the O atom, indicating that antibonding orbitals of CO have been populated. To uncover these orbitals, we retrieve their fingerprints on the electronic states of the surface-molecule

COMMUNICATION

moieties and we show them in Figure 5a-d. In the (101) case, although state a) is reminiscent of the $2\pi_y^*$ orbital of CO, state b) has bonding character with respect to the C-O bond and cannot be associated to $2\pi_x^*$. Indeed, very few states of the CO@TiO$_2$(101) system are C-O antibonding (Figure 5e), in line with the results of Ref. 6b. In contrast, for CO at (110), both c) and d) states have a nodal plane perpendicular to the C-O axis, give antibonding contribution to the C-O bond, and can be therefore traced back to the $2\pi_y^*$ and $2\pi_x^*$ LUMO of CO, respectively. States like c) and d) are an important fraction of the CO DOS for E> -9 eV and the dominant contribution at -7.5 eV (Figure 5f).
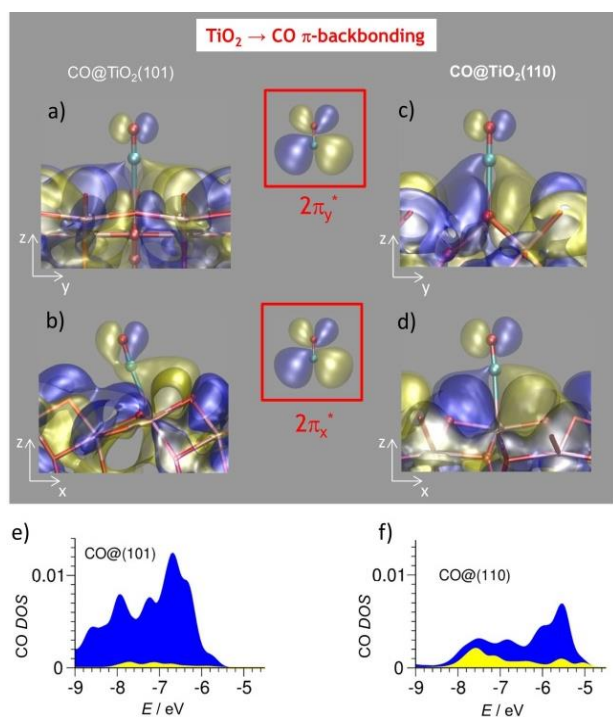

Figure 5. Orbitals showing the surface-CO π-interactions. For CO@TiO$_2$(101), only $2\pi_y^*$-backbonding is present (a); state b) has C-O bonding character. For CO@TiO$_2$(110), the orbitals c) and d) represent π-backbonding from the TiO$_2$(110) valence band levels (composed by O 2p states) to the $2\pi_y^*$ and $2\pi_x^*$ LUMO of CO (central insets), respectively. Positive lobes: blue, negative: yellow. Atom colors as in Figure 1. Bottom: Enlarged view of the CO DOS of Figure 3a,b for E>-9 eV, showing the total contribution of the states representative of π-backbonding (yellow) to the CO DOS (blue).

These data reveal that a donation-backdonation mechanism dominated by σ-bonding is operative in the adsorption of CO on TiO$_2$ surfaces. Both σ- and π-channels are more effective when CO is bound to Ti(4) sites at (110) facets compared to Ti(5) sites at (101) facets. Were σ-bonding the only contribution, the higher Lewis acidity of Ti(4) would result in a major strengthening of the C-O bond. However, backdonation from the TiO$_2$ valence band partially fills the CO LUMO. Such bond weakening effect is much greater for Ti(4) sites at (110) facets, where CO is perpendicular to the surface and close enough to the oxygen anions of the Ti(4) coordination sphere. Owing to such adsorption geometry, both $2\pi_x^*$, $2\pi_y^*$ orbitals of CO are suitably oriented and well

positioned for accepting electron density from TiO$_2$ (110) oxygen anions.
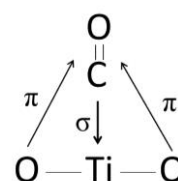
Scheme 1. σ- and π-contributions to the CO-TiO$_2$ interaction. The arrows indicate the direction of electron density donation. The standard, through-bond CO →Ti σ-donation is accompanied by π–backdonation from the neighboring surface oxygen anions (which are not bonded to CO).

Hence, the surprisingly lower νCO found for the more unsaturated Ti(4) site is the spectroscopic manifestation of a red-shifting process, *surface*-CO backdonation, much stronger at the (110) surface compared to the (101) one. This process is inherently different from standard backdonation, typical of transition metals and metal cations with d-electrons of suitable energy (Blyholder model).[7] In the present case, π-donation does not occur from the adsorbent Ti site (a d^0 cation), but from the *surface oxygen anions of its coordination environment*, which are not directly bonded to CO (Scheme 1). Furthermore, this new type of backdonation, here evidenced for the first time, is promoted by the Lewis acidity of the site *via* a strong Ti-C bond which draws the molecule close to the surface oxygen anions (see scheme 1), but is ruled by the structure and electronic states (band structure) of the specific facet, which determine the adsorption geometry. Therefore, donation-backdonation - and also Lewis acidity/reactivity - should be actually regarded as surface properties more than as local sites ones. In a broader perspective, this mechanism could be a general aspect of molecule-surface interactions in d^0-metal-oxides, which might provide insight to other phenomena, such as, for instance, the charge density increase reported for the oxygen atom of CO on top of TiO$_2$-B (100) surfaces.[23]

In summary, the CO-anatase TiO$_2$ interaction is: i) synergic - the greater the σ-donation to Ti, the stronger the π-backdonation to CO; ii) facet-specific – its extent depends on the exposed surface, and iii) collective - the surface is the actual electron donor and, via the oxygen anions of the Ti coordination environment, locally plays the Lewis-base role. As a consequence, TiO$_2$ reactivity, dominated by the Lewis acidity of unsaturated Ti sites, may also be tuned by the Lewis basicity of top layer oxygens.

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Entry for the Table of Contents

COMMUNICATION

Joint IR and modeling studies on TiO$_2$ nanoparticles reveal that the stretching frequency of adsorbed CO results from a synergic donation/backdonation mechanism, where the surface oxygen anions act as electron donors even if not directly bonded to the adsorbate (see image).
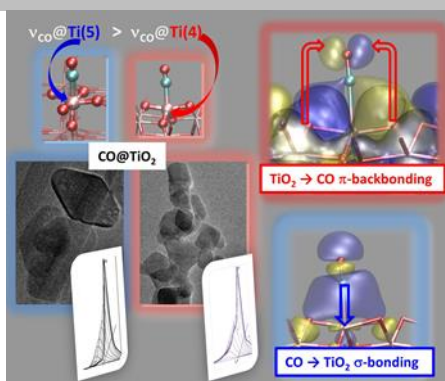
C. Deiana, E. Fois, G. Martra*, S Narbey, F. Pellegrino, G. Tabacchi*

Page No. – Page No.

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