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Surface structure of TiO₂ P25 nanoparticles: IR study of hydroxy groups on coordinative defect sites

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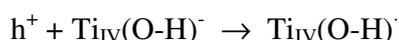
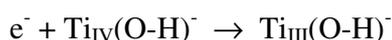
Abstract

Surface hydroxy groups are known to play a significant role in the photocatalytic behavior of TiO₂. The molecular or dissociative character of H₂O adsorption on titania is strongly affected by the local surface structure, but dissociation, producing –OH, should prevail on surface sites with a high degree of coordinative unsaturation. Here we report an IR investigation of hydroxy groups on low coordination sites of TiO₂ P25 (Degussa), a commercial titania powder considered a staple in the field of heterogeneous photocatalysis. The presence of coordinatively defective surface terminations well agrees with the roughness of the border of TiO₂ particles observed by high resolution transmission electron microscopy. Furthermore, IR spectra of adsorbed CO were used to probe the Lewis acidity of surface Ti⁴⁺ ions exposed after the removal of water molecules and hydroxy groups. Evidence for two additional types of surface cationic sites with respect those reported in the literature was found.

Keywords: TiO₂, P25 Degussa, surface hydroxy groups, coordinatively defective surface sites, adsorbed CO, TEM, IR spectroscopy.

Introduction

The importance of sustainable energy sources for power generation, the production of chemicals and the detoxification of air and water is elevating the role of TiO₂ as one of the key materials for the exploitation of chemical and -physical phenomena that can occur in semiconductors when exposed to solar radiation.¹⁻⁵ The photocatalytic performance of titania mainly depends on the separation and diffusion at the surface of the photogenerated e⁻/h⁺, but a significant role is also played by surface centers that control the interfacial transfer of such charges.^{6,7} In particular, surface hydroxylated centres have been proposed to act as trapping sites for both electrons and holes migrated to the surface, as in the following reactions:^{6,7}



Evidence for the hydroxy species resulting from these processes has been obtained,⁸ as well as for the actual influence of the surface hydroxylation on the photo-oxidation of phenol⁹ and the degradation of methylene blue.¹⁰ Furthermore, surface hydroxy groups are exploitable for the modification of the titania surface, as in the case of fluorination by OH⁻/F⁻ exchange.^{11,12}

The increased interest towards titania stimulated the development of a variety of preparation methods to obtain materials with better performance than commercial titania powders.¹³⁻¹⁶ Nevertheless, TiO₂ P25 (Degussa) represents a kind of landmark among these materials for photocatalytic applications and, in many instances, exhibits unsurpassed photocatalytic activity, as recently reported in a comparative work on 10 different TiO₂ powders.¹⁷

IR spectroscopy is widely employed for the investigation of surface hydroxy groups of catalysts and photocatalysts.¹⁸ The investigation of the IR features of surface -OH on titania powders has been the subject of many papers^{8,10,19-27} that have based the assignment of various νOH bands on the pioneering

work of Primet et al.²⁰ and Tsyganenko et al.²¹ Using these reports, νOH bands at frequencies higher than 3680 cm⁻¹ were assigned to linear hydroxy groups, while bands at lower frequencies were related to bridged -OH, the two species resulting from the dissociation of H₂O on pairs of coordinatively unsaturated Ti⁴⁺ and O²⁻ surface sites. However, more recent theoretical works have proposed that the dissociation of water on Ti⁴⁺-O²⁻ pairs exposed on the reactive anatase TiO₂ faces (001) results in the breaking of the Ti-O bond^{28,29} and with the production of two linear Ti-OH groups. These investigations also highlighted the dependence of the molecular and dissociative effects on the adsorption of H₂O on TiO₂ surfaces with different types of surface planes and amounts of water coverage. Furthermore, both experimental^{27,30} and theoretical³¹ investigations have pointed out the dissociative character of the adsorption of H₂O on coordinative defect sites as steps and corners, the amount of which should increase as the size of the TiO₂ particles decreases. However, depending on the local configuration, steps can be less reactive than flat surfaces.³¹

Despite such a rich panorama of research, a detailed study of the multicomponent νOH pattern exhibited by some types of TiO₂ nanoparticles, including TiO₂ P25,^{22,27,32} is still missing. A general assignment was proposed by Busca et al. for TiO₂ P25,²² and experimental data and theoretical calculations from Dzwigaj et al. explored the dependence of the νOH pattern on the morphology of two types of anatase TiO₂ particles, focusing on regular faces.³³ Furthermore, in those experiments water molecules were present on the surfaces, and most of the observed νOH bands were attributed to adsorbed H₂O. Notably, the investigation of structure-reactivity relationships of steps on anatase TiO₂ single crystals has been the subject of a combined experimental and theoretical study.^{31a} Unfortunately, to the best of our knowledge, no vibrational analyses were performed as part of such modeling.

To contribute to the elucidation of such stimulating matter, even more complex for nanoparticles exposing a variety of surface terminations, we adopted a selective approach, targeting the recognition of νOH bands that should be due to hydroxy species on coordinative defect sites and/or on poorly extended faces exposing Ti⁴⁺ in low coordination (e.g. the four-coordinated ones present on (110) anatase planes).

To assess the actual morphology of the borders of the TiO₂ particles, high resolution transmission electron microscopy was employed.

Although sites of these kinds represent a minor fraction of the surface centers, they belong to the category of surface defects that are responsible for much of the surface chemistry of oxides.^{34,35} Moreover, OH groups on coordinative defect sites are expected to be removed at higher temperature than those of regular planes and water molecules, allowing a selective observation of their IR stretching absorption bands. Conversely, water molecules, which are strongly adsorbed on Ti⁴⁺ cations through a coordinative interaction, and hydroxy groups on regular planes share a range of outgassing temperatures,²⁷ preventing an unequivocal observation of the stretching bands due to such OH groups only.

Furthermore, to assess the actual location of hydroxy groups on sites with different local structures, IR spectroscopy of adsorbed CO was employed to probe the Lewis acidity of Ti⁴⁺ sites originally occupied by OH species and H₂O molecules.

2. Experimental

2.1. Materials

The material investigated was TiO₂ P25, obtained from Degussa. As received, it exhibited a SSA_{BET} of ca. 55 m²·g⁻¹, which remained essentially unchanged under thermal treatment up to 773 K, but then decreased to ca. 40 m²·g⁻¹ when the temperature was raised to 873 K. This temperature represents the limit temperature before the anatase to rutile phase transformation occurs *in vacuo*.³⁶ For this reason, the spectroscopic study was carried out on samples treated at 873 K (in the IR cells, as reported in the next section) and then rehydrated by contact with 20 mbar of H₂O vapor for 60 min. This rehydration did not restore the initial SSA_{BET}, so changes of the intensity of the IR bands from increasing the temperature of subsequent treatments were no longer affected by changes in specific surface area.

H₂O and D₂O (99.90 % D, Euriso-top) were introduced onto the samples after several freeze-pump-thaw cycles and high purity CO (Praxair) was employed after liquid nitrogen trapping.

2.2. Methods

High resolution transmission electron microscopy (HR-TEM) images of the materials (powder grains “dry” dispersed on lacey carbon Cu grids) were obtained using a JEOL 3010-UHR microscope with an acceleration potential of 300 kV.

For **IR measurements**, the TiO₂ powder samples were pressed in self-supporting pellets and placed in quartz cells designed to carry out spectroscopic measurements at beam temperature (b.t., ca. 323 K; cell equipped with CaF₂ windows, optical path ca. 7 mm) or at low temperature (i.e., ca. 100 K) by cooling with liquid N₂ (cell equipped with KBr windows, optical path ca. 100 mm). Because of the high intensity of the bands due to CO adsorbed at low temperature, pellets with an “optical thickness” of ca. 10-15 mg·cm⁻² were used for this kind of measurement, whereas the “optical thickness” of the pellets used to collect spectra at b.t. was increased up to 20-30 mg·cm⁻². The cell was connected to a conventional vacuum line (residual pressure: 1×10⁻⁵ mbar) allowing all thermal treatments and adsorption–desorption experiments to be carried out *in situ*. A Bruker IFS 28 spectrometer (resolution: 2 cm⁻¹; detector: MCT) was employed for the spectra collection. Depending on the case, from 150 to 500 scans were accumulated to obtain a good signal to noise ratio.

Before IR measurements, the samples were outgassed at a temperature ranging from b.t. to 873 K for 60 min. For outgassing temperatures ≥ 573 K, samples were placed in contact with O₂ (6 mbar) at the same temperature for 60 min after initial outgassing. Then, the pellets were cooled to 473 K in O₂ and further cooled down to room temperature under outgassing. For the sake of simplicity, in the text this multi-steps treatment will be simply referred to as “outgassing” or “pre-outgassing” (when followed by CO adsorption). In all cases, at the end of the procedure, the samples were white in color, as expected for stoichiometric (fully oxidized) TiO₂.

To remove the slope due to scattering from the νOH and $\delta\text{H}_2\text{O}$ regions, at the end of the IR measurements at room temperature, the TiO_2 pellet was re-treated at 873 K, contacted with 20 mbar D_2O and outgassed at b.t., and its spectrum was used as the background for data elaboration (see Supporting Information, Figure S1). In the case of the spectra of adsorbed CO, the spectrum of the sample before CO admission was subtracted as the background.

Resolution of subbands present in the spectra of adsorbed CO was achieved by using the “Curve fit” utility of OPUS 5.0 (Bruker Optic GmbH). The fits were optimized by using a local least squared method.

3. Results and discussion

3.1. Surface morphological features

TEM inspections evidenced a wide heterogeneity in the size of the titania particles, ranging from ca. 10 to 50 nm (Figure 1A), in agreement with data previously reported by Ohno et al.³⁷ As for the shapes, some of the observed profiles were easily recognized as bidimensional projection of truncated bipyramids with the main axis (almost) parallel to the image plane, as displayed by 3D schemes. For most of the shapes, however, the contours of the projections could be due to more isometric particles. A different possibility was that such contours resulted from the projection of bipyramids (or capped prisms) with the main axis perpendicular to the image plane. However, all these morphologies were in agreement with those proposed in theoretical and experimental reports dealing with pure anatase powders.^{28,33 38} At high magnification, fringes due to diffraction contrast appeared resolved (Figure 1B), supporting the crystalline nature of TiO_2 particles. A detailed analysis of such a pattern for crystallographic indexing of exposed extended surfaces is outside the scope of this work, but has been among the subjects of previous investigations, where the exposure of planes of the (101) and (001) type

was proposed.^{32,39} Here we focused on the roughness, at the level of a few reticular steps, of part of the borders of the particles (Figure 1B,B',B''), that indicated the presence of a variety of local terminations rich in corners, steps and edges, where the coordinative unsaturation of exposed lattice atoms should be higher than on more regular and flat surfaces.

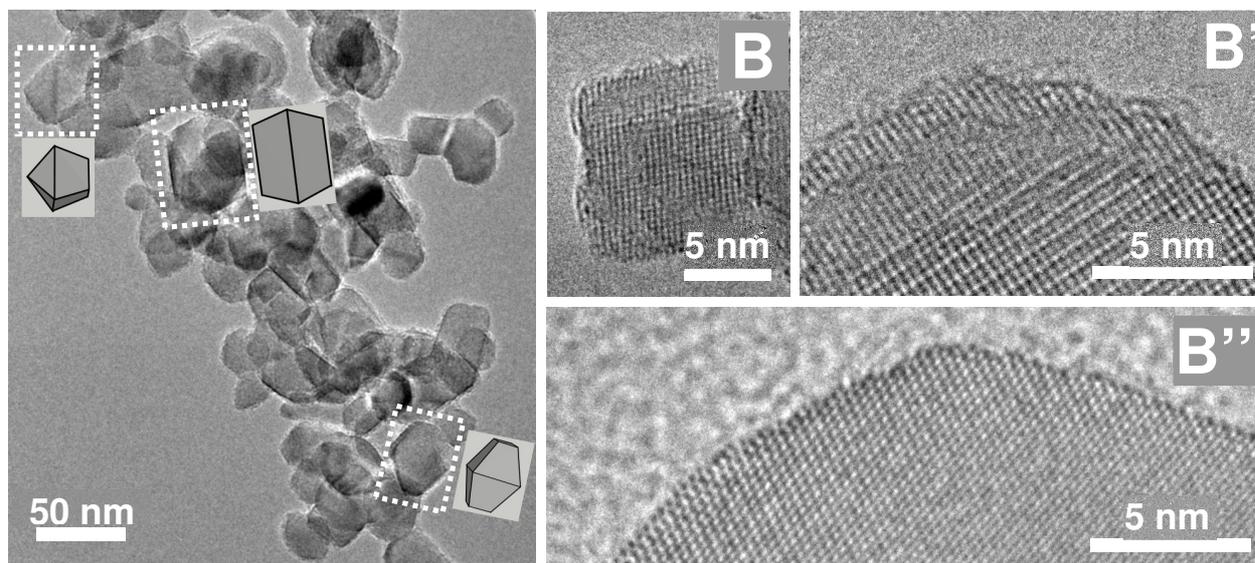


Figure 1. TEM images representative of size and morphology of TiO₂ P25. Panel A: overall view (original magnification: ×80 k). Panels B,B',B'': zoomed view of some rough border regions (original magnification: ×500 k).

3.2. Dehydration, dehydroxylation and probing of coordinatively unsaturated surface cations by CO adsorption

3.2.1 TiO₂ samples outgassed up to 773 K

As reported in the Introduction, this work was devoted to hydroxy groups on coordinative defective sites, the νOH bands of which are more clearly observed after outgassing at high temperature. Nevertheless, for the sake of completeness, the evolution of the IR pattern due to surface hydration

species by progressive outgassing from beam temperature was monitored, as well as the spectra of CO adsorbed at 100 K after each outgassing step were collected. A detailed analysis of these data was outside the scope of the paper, and the comments were limited to possible open questions and to the occupancy of surface sites by hydroxy groups or water molecules.

3.2.1.1. Evolution of bands due to hydroxy groups and adsorbed water

Figure 2 shows the spectra of TiO₂ outgassed up to 773 K in the $\nu(\text{OH})$ (Section A) and $\delta\text{H}_2\text{O}$ (Section B) ranges, which exhibited a general trend quite similar to that reported by Morterra in his seminal work on an anatase sample prepared *via* the chloride.²⁷

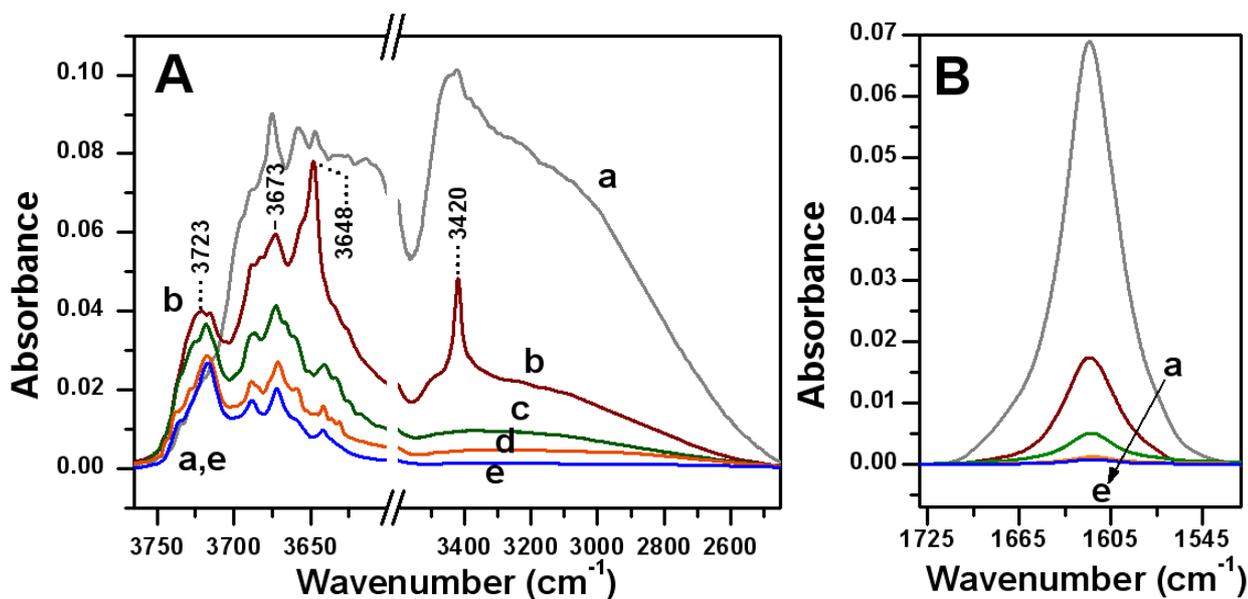


Figure 2. IR spectra in the $\nu(\text{OH})$ and $\delta\text{H}_2\text{O}$ regions (section A and B, respectively) of TiO₂ P25 outgassed for 60 min at: a) beam temperature, i.e. ca. 323 K; b) 473; c) 573; d) 673 and e) 773 K. On the X axis, the scale has been changed at 3600 cm^{-1} , to zoom the region at higher frequency. The gap on the axis is just of 1 cm^{-1} .

After degassing at beam temperature (curve a) the region at high frequencies was dominated by broad and complex absorption spread over a range from 3600 to 2500 cm^{-1} , due to $-\text{OH}$ oscillators involved in H-bonds, and accompanied by a series of narrow and partly resolved peaks/subbands in the 3600-3750 cm^{-1} range, related to $-\text{OH}$ groups experiencing weaker intermolecular interactions (Figure 2A). In experimental studies, bands in the later range have been mostly assigned to hydroxy groups, whereas undissociated water molecules, coordinatively adsorbed on surface Ti^{4+} ions, mainly contributed to the 3600-2500 cm^{-1} absorption,²⁷ other than produce the $\delta\text{H}_2\text{O}$ band at ca. 1620 cm^{-1} (Figure 2B). However, more recent theoretical investigations proposed that H_2O adsorbed at high coverage, apparently not involved in H-bonds, should absorb in the 3750-3600 cm^{-1} range.²⁸ Nevertheless, the number of components in this range (at least 9, considering maxima and shoulders) indicated the presence of several types of surface sites bearing hydroxyl groups and adsorbed H_2O molecules.

The decrease in integrated intensity of the $\delta\text{H}_2\text{O}$ band after outgassing at 473 K (Figure 2B, b) monitored the removal of approximately 75% of the adsorbed H_2O molecules. Water desorption and condensation of hydroxy groups were also responsible for the decrease in intensity of the νOH pattern that occurred to a much higher extent for the broad 3600-2500 cm^{-1} band than for the set of sharp 3750-3600 cm^{-1} peaks. This latter now exhibit a main peak at 3648 cm^{-1} , asymmetric towards the lower frequency side and with a shoulder at 3655 cm^{-1} . Additionally, another component at 3673 cm^{-1} with subbands at 3690 cm^{-1} , and a new band with maximum at 3723 cm^{-1} , resulting from the overlap of several components, appeared. This complex signal was assigned to O-H oscillators initially involved in H-bonding (and then absorbing at lower frequencies) with hydroxyl groups/water molecules that were removed by outgassing. Noticeably, a quite narrow band was now observed at 3420 cm^{-1} , still superimposed on a broad absorption. This band was supposed to be characteristic of the rutile phase present in the P25⁸ but was also observed for a pure anatase sample.²⁷ In this last case, it was assigned to coordinated water species on the basis of the similar evolution in dependence on the outgassing

temperature with respect to the $\delta\text{H}_2\text{O}$ band. Conversely, in a more recent paper, this component was supposed to be due to hydroxy groups playing a special role in the photocatalytic behavior of the P25, but unfortunately, the $\delta\text{H}_2\text{O}$ spectral range was not reported.¹⁰

In the present case, outgassing at 573 K (Fig. 2A,B, curves c) resulted in the depletion of the 3420 cm^{-1} band and in a decrease in intensity of the broad feature below, while the $\delta\text{H}_2\text{O}$ band appeared significantly weaker. This behavior might support the assignment of the 3420 cm^{-1} signal to water molecules. However, it must be considered that two νOH absorptions were expected for H_2O molecules and that a partner signal must be identified. In addition, the location of the considered band was in the range typical for OH oscillators involved in H-bonds, and such interactions usually produce a significant broadening of the absorption profile (increasing as the frequency of the maximum is decreased). Furthermore, none of the frequencies calculated by Arrouvel et al.²⁸ for adsorbed H_2O fit with the band at 3240 cm^{-1} . We propose that the assignment of this component remains a matter of debate for future experimental and theoretical investigations.

As for the set of signals at higher frequencies, the main effect of outgassing at 573 K was the depletion of the 3648 cm^{-1} peak, accompanied by an overall decrease in intensity of the other components. Subsequent outgassing at increasing temperatures up to 773 K left only traces of the broad absorption in the 3600-2600 cm^{-1} region and resulted in a progressive decrease in intensity of the 3750-3600 cm^{-1} pattern (Figures 2A). As for molecular water, it must be considered that outgassing at $T \geq 673$ K should result in a complete desorption of H_2O molecules. Nevertheless, a very weak $\delta\text{H}_2\text{O}$ was still observed. The actual nature due to water of this signal was proved by subsequent contact with D_2O vapor (not shown). The presence of H_2O molecules should be ascribed to re-adsorption of trace amounts of water released from the inner walls of the cell (that were not fully heated during outgassing) once the sample was cooled down to beam temperature. Noticeably, despite the presence of adsorbed H_2O , no signal was present in the 3600-2600 cm^{-1} range for the sample outgassed at 773 K (Fig. 2B, e). This feature will be commented on in the section devoted to the spectra collected after outgassing at higher

temperatures. Focusing on the 3750-3600 cm^{-1} pattern (Fig. 2A), no significant changes in the relative intensity of the various components occurred by outgassing at 773 K, except for the more severe suppression of the subband at $\nu \geq 3725 \text{ cm}^{-1}$ (Figure 2A, d).

To assess the actual level of coordinative unsaturation of surface Ti^{4+} centers that were initially occupied by water and hydroxyl groups, IR spectra of CO adsorbed on TiO_2 outgassed at increasing temperatures were then collected. The results obtained are reported and commented on in the next section.

3.2.1.2. IR spectra of CO adsorbed at 100 K on samples pre-outgassed up to 773 K

The adsorption of CO at 100 K on TiO_2 pre-outgassed at increasing temperatures from 473 to 773 K resulted in the appearance of a dominant peak at 2179 cm^{-1} in the IR spectra, that exhibited some increase in intensity as the pre-outgassing temperature was increased (Figure 3).

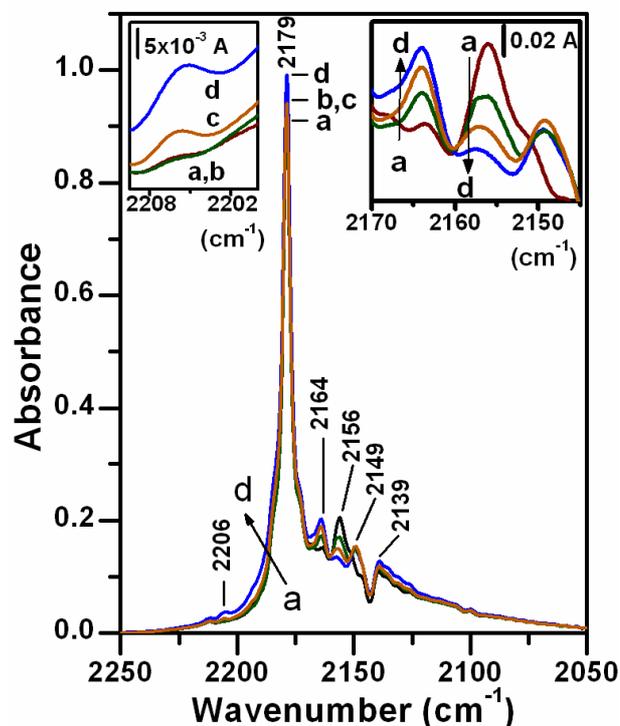


Figure 3. IR spectra of CO adsorbed at ca. 100 K on TiO_2 P25 outgassed at: a) 473; b) 573; c) 673 and d) 773 K. Insets: zoomed views of the 2210-2000 and 2170-2145 cm^{-1} ranges.

Furthermore, by decreasing the CO coverage, the maximum shifted to ca. 2188 cm^{-1} (see Supporting Information, Figure S2), which usually resulted from the weakening of interactions among parallel and close oscillators.^{40,41} All these features were typical of CO molecules adsorbed on penta-coordinated Ti^{4+} ions (hereafter β sites, following the nomenclature proposed by Hadjiivanov et al.⁴⁰) exposed on (010) [isostructural with (001)] and (101) [isostructural with (011)] faces.^{33,39,40} By considering that:

- i) pre-outgassing at 473 K removed ca. 75 % of the initially adsorbed water while affecting the hydroxy groups to a significantly lesser extent (Figure 2);
- ii) the peak due to CO adsorbed on β sites exhibited only a limited increase in intensity from increasing pre-outgassing temperatures over 473 K,

it can be concluded that an overwhelming portion of the β sites were initially occupied by H_2O molecules.

Conversely, the weaker band at 2164 cm^{-1} , due to CO on penta-coordinated Ti^{4+} ions on (001) planes (γ sites),⁴⁰ increased progressively in intensity as the pre-outgassing temperature was increased (Figure 3, right inset), indicating that such sites should have been originally occupied also by hydroxy groups. This feature is in agreement with the calculations performed by Arrouvel et al.,²⁸ that indicated a dissociative character for the adsorption of H_2O on (001) anatase surfaces. Moreover, hydroxy groups resulting from the dissociation on such surfaces were expected to contribute to the high frequency part of the νOH pattern, and in the present case subbands at $\nu > 3730 \text{ cm}^{-1}$, decreasing in intensity by outgassing at 473-773 K, were present (Fig. 2A).

Also hydroxy groups remaining on the surface acted as sites for CO adsorption, producing the weak νCO band at ca. 2156 cm^{-1} , that decreased in intensity as the pre-outgassing temperature increased (Fig. 3, right inset). Accordingly, the perturbation of the νOH pattern in the 3750-3600 cm^{-1} range occurred (see Supporting Information, Figure S3).

Two other νCO components appeared at 2149 and 2139 cm^{-1} (Fig.3). The former one was not observed in previous studies. Here, it is tentatively assigned to CO in interaction with surface Ti^{4+} ions

with a very weak Lewis acid character, also on the basis of the results obtained dosing CO on samples outgassed at higher temperature (*vide infra*). Conversely, the band at 2139 cm⁻¹ is the typical feature due to physically adsorbed CO.^{39,40} This was the only signal increasing in intensity by increasing the pressure of CO over 40 mbar (not shown).

Pre-outgassing at 673 and 773 K resulted in a slight increase of the main peak at 2179 cm⁻¹, monitoring the exposure to CO of additional β sites. Moreover, a weak component at 2206 cm⁻¹ was noticeable, due to CO adsorbed on α sites, i.e., surface four-coordinated Ti⁴⁺ ions, such those exposed on (110) and (113) surfaces, as well as on some edges, such as 100×010, 100×110 and 101×110.⁴⁰ These surfaces, when hydrated, have been proposed to carry OH groups rather than undissociated water molecules.²⁸ On the basis of the calculations by Arrouvel et al.,²⁸ OH on (110) surfaces should be responsible for a component around 3725 cm⁻¹ in the spectra in Figure 2A.

However, the variety of surface terminations on the rough parts of the particle terminations suggested the possible presence of several types of local structures that could expose Ti⁴⁺ and O²⁻ acid-base pairs able to dissociate H₂O molecules, producing a multicomponent vOH pattern. To elucidate this question, the outgassing temperature was increased stepwise up to 873 K, the maximum temperature attainable without a significant occurrence of the anatase to rutile phase transformation, again probing with CO the Ti⁴⁺ sites rendered coordinative unsaturated by dehydroxylation.

3.2.2. TiO₂ samples outgassed up to 873 K

TiO₂ was outgassed at 823 and 873 K and the related spectra in the vOH (sample *in vacuo*) and vCO ranges [dealing with CO (150 mbar) adsorbed at beam temperature], are reported in Figure 4 (sections A and B, respectively). The spectra obtained for TiO₂ outgassed at 773 K are also shown, for the sake of completeness.

As reported above, trace amounts of water molecules were reabsorbed on the sample after outgassing, as proved by the presence of an extremely weak δ H₂O signal (Figure 4A, inset). Conversely,

no signals were detected in the 3600-2600 cm^{-1} region, so it was concluded that the observed $\nu(\text{OH})$ absorptions due to water molecules should fall in the 3750-3600 cm^{-1} range. In actuality, calculation for high water coverage produced stretching frequencies at 3710 cm^{-1} for H_2O on (100) faces ($8.2 \text{ H}_2\text{O} \cdot \text{nm}^{-2}$) and at 3665 and 3646 cm^{-1} for H_2O on (101) faces ($10.1 \text{ H}_2\text{O} \cdot \text{nm}^{-2}$).²⁸ Such values, much higher than expected for adsorbed water molecules, were explained on the basis of intermolecular repulsions that hindered H-bonding. Dipole-dipole repulsions were also proposed to be an origin for the $\nu(\text{OH})$ upward shift observed in the HREELS spectrum by increasing H_2O coverage on (110) rutile single crystals.³⁰ In the present case, however, the amount of adsorbed H_2O was rather small (the integrated intensity of the $\delta\text{H}_2\text{O}$ bands in the insets of Figure 4A was ca. 0.5 % of the band originally observed after outgassing at b.t., see Figure 2B, curve a). Therefore, the hypothesis of interactions between adsorbed H_2O molecules could only hold considering a highly heterogeneous distribution of adsorbed water molecules, for instance forming patches on the external surface/first layers of the TiO_2 pellet first encountered during their adsorption. In support of this claim, a limited diffusion for a gaseous probe dosed at low pressure within a pelletized powder was previously reported for CO .⁴² A different possibility for this phenomenon is the adsorption of H_2O on sites with local structure that oriented the molecules with their two OH bonds pointing out from the surface and caused them to experience a very weak interaction with neighboring surface O^{2-} or OH sites.

However, for the scope of this work, two points must be stressed:

- i) the amount of water appeared to be essentially the same after all treatments in the range 773-873 K (Figure 4A, inset), and then also the bands due to their stretching modes should contribute to the same extent to the three $\nu(\text{OH})$ spectra in Figure 4A. Hence, the decrease in intensity of such patterns by increasing the outgassing temperature should have been due to the removal of hydroxy groups;
- ii) the $\delta\text{H}_2\text{O}$ exhibited a very weak intensity, and then also the partner stretching modes, being the protons not involved in strong H-bonding, should exhibit an intensity of the same order of magnitude.⁴³ Hence, they contributed to a very minor extent to the $\nu(\text{OH})$ absorptions.

It can be then concluded that the signals at 3736, 3717, 3688, 3672, 3659 and 3642 cm^{-1} present after outgassing at 773 K are essentially due to hydroxy groups. Furthermore, the multiplicity of components due to both linear ($\nu\text{OH} > 3680 \text{ cm}^{-1}$) and bridged ($\nu\text{OH} < 3680 \text{ cm}^{-1}$) OH indicates the presence of more than one local structure for each type of hydroxy species.

The overall pattern obtained in the present case appeared quite similar to that found by Dzwigaj et al.³³ after dehydration at 693 K of another type of pure anatase commercial TiO_2 , where, conversely, most of the signal were assigned to the presence of water. Unfortunately, an estimation of the amount of H_2O molecules is rather difficult, as the $\delta\text{H}_2\text{O}$ spectral range was not reported.

Outgassing at $T > 773 \text{ K}$ resulted in a decrease in intensity of the pattern, indicating the removal of part of these hydroxy groups. The resulting coordinative unsaturation of Ti^{4+} sites deprived of such ligands was then tested by IR spectroscopy of adsorbed CO. As reported in the Experimental section, CO was adsorbed at beam temperature (ca. 323 K) to optimize the observation of the weak νCO components at frequencies $\geq 2190 \text{ cm}^{-1}$. Under such experimental conditions, CO was able to probe all α sites, but only a part of the β ones, termed by Hadjiivanov as β' .⁴⁰ The difference in the adsorption capacity of CO on β' and the other β sites (termed as β'') was proposed to have an induced character, i.e., the occurrence of a decrease in Lewis acidity of still unoccupied Ti^{4+} ions (the β'' sites) once CO was adsorbed on surface cations (the β' sites).⁴⁰ Nevertheless, all β sites were monitored in proper measurements where CO adsorption was carried out at 100 K, indicating that pre-outgassing temperatures $\geq 773 \text{ K}$ did not result in an increase in intensity of the peak at 2179 cm^{-1} (See Supporting Information, Figure S3). On the contrary, this peak exhibited a slightly lower intensity, whereas the band at 2149 cm^{-1} increased in intensity, suggesting the occurrence of an inward relaxation for some surface cations,⁴⁴ resulting in a decrease on their Lewis acidity.

Focusing on CO adsorbed at beam temperature, a progressive increase in intensity of the 2206 cm^{-1} band due to CO adsorbed on α sites occurred by increasing the pre-outgassing temperature, as well as a slight broadening of the peak due to CO on β' sites. This signal also exhibited some decrease in

intensity for pre-outgassing temperatures ≥ 823 K (Figure 4B). Therefore, the combination of spectral data in Figures 4A and B indicated that the vOH pattern in the $3750\text{-}3600\text{ cm}^{-1}$ range was due to -OH groups sitting on sites not located on extended, regular faces exposing penta-coordinated Ti^{4+} ions of the β type. Furthermore, the decrease in integrated intensity of only ca. 50% by increasing the outgassing temperature from 773 to 873 K indicated that these OH groups are bound quite strongly to the surface.

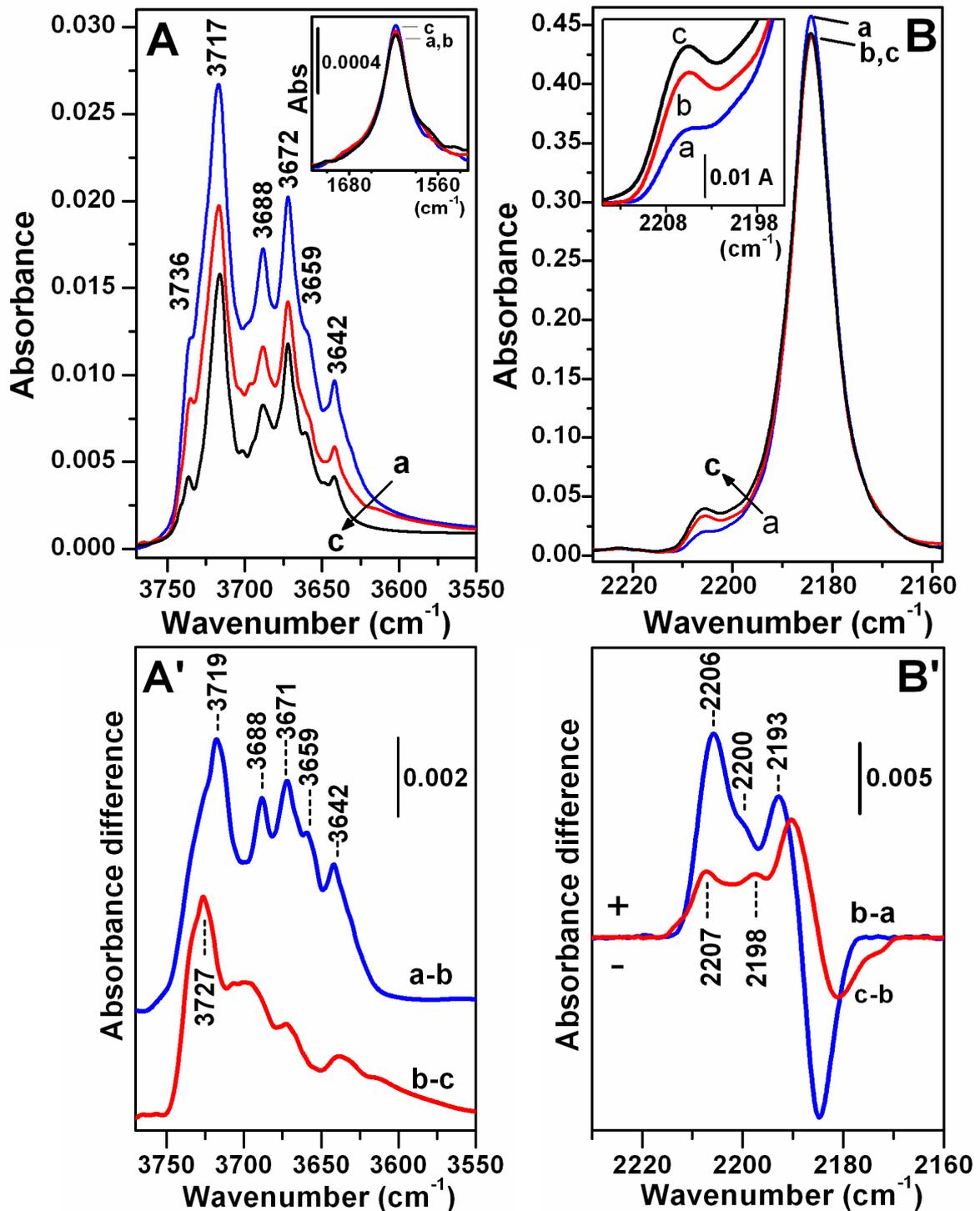


Figure 4. Upper panels: IR spectra in the νOH (section A) and νCO (section B) regions of TiO_2 P25 stepwise outgassed at $T \geq 773$ K and contacted at beam temperature with 150 mbar of CO. In both sections, lettering is as follows: a) $T_{\text{outg.}} = 773$ K; b) $T_{\text{outg.}} = 823$ K; c) $T_{\text{outg.}} = 873$ K. Insets: zoomed views of the $\delta\text{H}_2\text{O}$ (section A) and $2215\text{-}2195\text{ cm}^{-1}$ (section B) ranges. Lower panels: results of the subtraction between spectra in upper panels. In sections A' (νOH region) lettering is as follows: a-b) difference between spectra of the sample outgassed at 773 K (a) and at 823 K (b); b-c) difference between spectra of the sample outgassed at 823 K (b) and at 873 K (c). In section B' (νCO region) lettering is as follows: b-a) difference between spectra of CO (150 mbar) adsorbed on the sample outgassed at 823 K (b) and at 773 K (a); c-b) difference between spectra of CO (150 mbar) adsorbed on the sample outgassed at 873 K (c) and at 823 K (b).

The observed decrease in intensity of the νOH pattern was accompanied by some change in the relative intensity of the various components. To extract the pattern due to hydroxy groups removed by rising the outgassing temperature ($T_{\text{outg.}}$) from 773 to 823 K and then to 873 K, the difference between the spectra recorded after consecutive outgassing temperatures was calculated (Figure 4A').

The spectral profile due to OH removed by increasing $T_{\text{outg.}}$ at 823 K (curve "a-b") appeared rather similar to the pattern observed after outgassing at 773 K (Figure 4A, a), indicating that the removal of hydroxy groups occurred via a classical condensation between linear and bridged OH.

Conversely, outgassing at 873 K seemed to remove OH groups responsible for the band at 3726 cm^{-1} , likely terminal OH groups, to a large extent. It is proposed that such groups could have been originated through a dissociation mechanism similar to that proposed for H_2O on an (001) anatase face,^{28,29} resulting in the breaking of the Ti-O bond. If this mechanism can occur for some type of $\text{Ti}^{4+}\text{-O}^{2-}$ in coordinative defective positions, neighboring linear Ti-OH groups might be produced, that will condense, restoring the Ti-O bond, at a due temperature. A different possibility was proton migration, as proposed for the last stages of dehydroxylation of MgO.⁴⁵

Furthermore, minor components at lower frequency appeared quite broad and ill defined, suggesting the presence, in low amount, of families of hydroxy groups, each constituted by OH oscillators located in slightly different local structures. This feature could be another consequence of the roughness of the borders of the TiO₂ particles observed, on a larger scale, by TEM.

The subtraction between spectra of CO adsorbed on TiO₂ outgassed at two subsequent steps was also carried out. In this case, the signal increased in intensity by increasing the pre-outgassing temperature, and then, for each pair of spectra considered, the spectrum due to CO adsorbed on the sample outgassed at higher temperature was considered as minuend, and the other was considered as subtrahend. The results are reported in Figure 4B' and show the νCO signals due to probe molecules adsorbed on Ti⁴⁺ ions deprived of –OH ligands by increasing the outgassing temperature from 773 to 823 K (curve “b-a”) and from 823 to 873 K (curve “c-b”). As expected, a component at 2006-2007 cm⁻¹ was present (the largest signal by far in the case of the sample outgassed at 823 K, curve a), due to CO adsorbed on α cationic sites, but additional ones were also observed at 2200-2198 cm⁻¹ and 2193-2190 cm⁻¹. However, this last signal appeared partly superimposed on a negative band at 2184-2181 cm⁻¹, which may have affected its actual position. The negative part of the signal indicated the disappearance of some β' sites that could have resulted from inward relaxation or from conversion in cationic centers with a higher degree of coordinative unsaturation by removal of an hydroxy group.

Other than from the difference spectra, evidence of the presence of more than one νCO component in the 2210-2185 cm⁻¹ range was provided by the spectra collected over decreasing CO coverage. For the sake of brevity, the complete set of data is shown only for TiO₂ pre-outgassed at 873 K (Figure 5), whereas a comparison among selected spectra collected for TiO₂ pre-outgassed at increasing temperatures is reported in the Supporting Information (Figure S4).

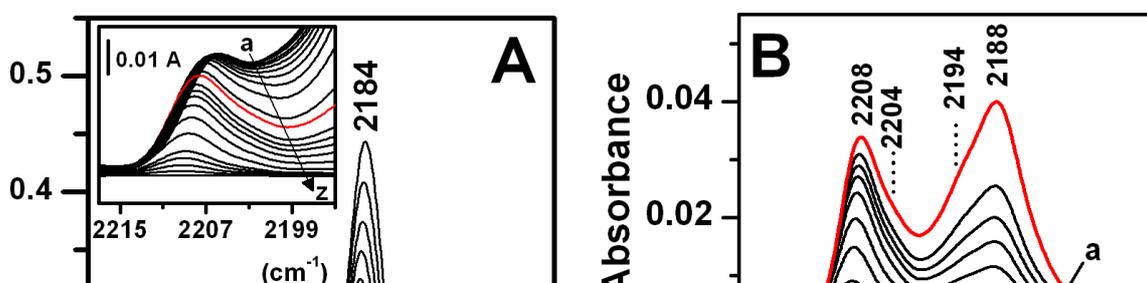


Figure 5. IR spectra of CO adsorbed at beam temperature on TiO₂ P25 outgassed at 873 K for 60 min. Section A: progressively decreasing coverages from (a) 150 mbar CO to (z) outgassing for 5 min at beam temperature. In red is the spectrum taken in the presence of 3 mbar CO. Inset: zoomed view of the 2217-2195 cm⁻¹ range. Section B: zoomed view of the spectra taken at progressively decreasing CO coverages from (a) 3 mbar CO (red line) to (m) outgassing for 5 min at beam temperature. Section B': components (solid grey lines) and simulated total profile (dashed grey line) resulting from the fitting of the spectrum taken in the presence of 3 mbar CO (red line, upshifted for the sake of clarity).

Focusing on Figure 5A, the progressive removal of CO produced a preferential decrease in intensity of the main band at 2184 cm⁻¹ with respect to the components at higher frequencies, reflecting the

weaker interaction of CO with β' sites than other surface cationic sites active toward CO adsorption at beam temperature. The main band also up-shifted from 2184 to 2188 cm^{-1} as a consequence of the decrease in adsorbate-adsorbate interactions. Such interactions (limited to the static type) also involved CO on α sites (Figure 5A, inset), as the related component slightly upshifted. This signal then started to decrease in intensity and moved to 2208 cm^{-1} as CO outgassing progressed.

Starting from an equilibrium pressure of 3 mbar of CO, other than the remaining part of the 2188 cm^{-1} and 2208 cm^{-1} bands, two shoulders at ca. 2204 and 2194 cm^{-1} can be observed (Figure 5B). Indeed, a minimum of four components was necessary to fit the experimental spectra. As an example, the fitting of the spectrum collected in the presence of 3 mbar of CO is reported in Figure 5B'.

The component at 2194 cm^{-1} appeared quite close to the location indicated for the singleton of CO adsorbed on β sites^{39,40} but was distinct from the signal at 2188 cm^{-1} that resulted from the evolution of the band due to such species. Furthermore, the 2194 cm^{-1} component was even less defined with respect to the 2188 cm^{-1} peak in the spectrum of CO adsorbed on TiO_2 outgassed at 773 K (see Supporting Information, Figure S4), indicating that these signals are due to CO on sites that retained hydroxy groups more strongly than the β sites.

The entire collection of data presented here indicated that two other types of cationic centers, one with a Lewis acidity slightly lower than α sites, and the other with a Lewis acidity slightly higher than β sites, are present on the surface of the TiO_2 P25. Moreover, the differences in the profiles of the differential spectra (Fig. 4B) and the broadness of the 2204 and 2194 cm^{-1} components of the fit of the direct spectra (Fig. 5B') suggested the presence of some structural heterogeneity among such cationic sites.

By assuming that the molar extinction coefficient of adsorbed CO species is independent of frequency changes in the 2220-2180 cm^{-1} interval,^{46,47} the ratio among integrated intensities indicated that the amount of these cationic sites is of the same order than α sites.

Finally, it must be considered that CO was able to probe only cationic sites, whereas it is essentially insensitive to the coordinatively unsaturated surface oxygen sites that resulted from the deprotonation of

bridging hydroxy groups (where the oxygen atoms belonged to the surface lattice) created from condensation between linear and bridging OH groups (the reverse of the dissociation of H₂O on a Ti⁴⁺-O²⁻ pair). Spectroscopic experiments with other kinds of probes (e.g., CHCl₃ and acetylenes⁴⁸) will be the subject of future work.

4. Conclusions

The data obtained for outgassing temperatures ≤ 773 K put in evidence that the overwhelming majority of the surface of TiO₂ P25 that expose β cationic sites adsorbed H₂O molecules undissociatively. Moreover, confirmative evidence of the presence of hydroxy groups on γ sites on (001) faces was obtained.

As for the main target of the investigation, the ν OH pattern related to hydroxy species on surface sites under low coordination conditions was recognized. The number of observed components well accounted for the heterogeneity seen for the defective surface terminations suggested by the TEM images. Notably, evidence for the presence of two types of surface Ti⁴⁺ ions with Lewis acid strength intermediate between the already known α and β cationic sites was also obtained.

Therefore, the work carried out provided experimental vibrational frequencies of intrinsic (i.e., hydroxy groups) and extrinsic (i.e., CO) probes of TiO₂ surface sites in low coordination. In particular, more coordinatively unsaturated cationic sites were probed by both hydroxy groups and CO. These results could then represent a database which should significantly help in selecting/refining theoretical models in the elucidation of the local structures of such sites, or, at least, of a part of them. This will be the subject of the extension of this work.

If successful, this approach will provide structural insight on the surface structure of TiO₂ nanoparticles that could be conveniently compared with those obtained for well-characterized coordinative defect sites on stepped titania single crystals.³¹

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References

- [1] Matsuoka, M.; Kitano, M.; Takeuchi, M.; Tsujimaru, K.; Anpo, M.; Thomas, J.M. *Catal. Today* **2007**, *122*, 51-61 and references therein.
- [2] Palmisano, G.; Augugliaro, V.; Magliaro, M.; Palmisano, L. *Chem. Commun.* **2007**, 3425-3437 and references therein.
- [3] Serrano, E.; Rus, G.; García-Martínez, *Renew. Sust. Energ. Rev.* **2009**, *13*, 2373-2384 and references therein.
- [4] Hochbaum, A.I.; Yang, P. *Chem. Rev.* **2010**, *110*, 527-546 and references therein.
- [5] Kalyanasundaram, K.; Graetzel, M. *Curr. Opin. Biotechnol.* **2010**, *21*, 298-310 and references therein.
- [6] Serpone, N., Pelizzetti, E., Eds *Photocatalysis: Fundamental and Applications*: Wiley-Interscience: New York, 1989.
- [7] Linsebliger, A.L.; Lu, G.Q.; Yates, J.T., Jr. *Chem. Rev.* **1995**, *95*, 735.
- [8] Szczepankiewicz, S.; Colussi, A.J.; Hoffman, M.R. *J. Phys. Chem.* **2000**, *104*, 9842-9850.
- [9] Palmisano, L.; Schiavello, M.; Sclafani, A.; Martra, G.; Borello, E.; Coluccia, S. *Appl. Catal. B: Environmental* **1994**, *3*, 117-132.
- [10] Du, P.; Bueno-López, A.; Verbaas, M.; Almeida, A.R.; Makkee, M.; Moulijn, J.-A.; Mul, G. *J. Catal.* **2008**, *260*, 75-80.
- [11] Maurino, V.; Minero, C.; Mariella, G.; Pelizzetti, E. *Chem. Commun.* **2005**, 2627-2629.
- [12] Minella, M.; Faga, M.G.; Maurino, V.; Minero, C.; Pelizzetti, E.; Coluccia, S.; Martra, G. *Langmuir*, **2010**, *26*, 2521-2527.

- [13] Kondo, J.N.; Yamashita, T.; Nakajima, K.; Lu, D.; Hara, M.; Domen, K. *J. Mater. Chem.*, **2005**, *15*, 2035-2040.
- [14] Buonsanti, R.; Grillo, V.; Carlino, E.; Giannini, C.; Curri, M.L.; Innocenti, C.; Sangregorio, C.; Achterhold, K.; Parak, F.G.; Agostiano, A.; Cozzoli, P.D. *J. Am. Chem. Soc.* **2006**, *128*, 16953-16970.
- [15] Kitano, M.; Matsuoka, M.; Ueshima, M.; Anpo, M. *Appl. Catal. A: General* **2007**, *325*, 1-14.
- [16] Centi, G.; Passalacqua, R.; Perathoner, S.; Su, D.S.; Weinberg, G.; Schlögl, R. *Phys. Chem. Chem. Phys.* **2007**, *9*, 4930-4938.
- [17] Ryu, J.; Choi, W. *Environ. Sci. Technol.* **2008**, *42*, 294-300.
- [18] Busca, G. In *Metal Oxide Catalysis*, Jackson, D., Hargreaves, J.S.J., Eds.; Wiley-VCH, Weinheim, 2009, Vol. 1., p. 95-176.
- [19] Erdem, B.; Hunsicker, R.A.; Simmons, G.W.; Sudol, E.D.; Dimonie V.L.; El-Aasser, M.S. *Langmuir* **1991**, *17*, 2664-2669.
- [20] Primet, M.; Pichat, P.P.; Mathieu, M.V. *J. Phys. Chem.* **1971**, *75*, 1216-1220.
- [21] Tsyganenko, A.A.; Filimonov, V.N. *J. Mol. Struct.* **1973**, *19*, 579-589 and reference therein.
- [22] Morterra, C.; Chiorino, A.; Boccuzzi, F.; Fiscaro, E. *Z. Phys. Chem. Neue Folge* **1982**, *124*, 211-222.
- [23] Busca, G.; Saussey, H.; Saur, O.; Lavalley, J.C.; Lorenzelli, V. *Appl. Catal.* **1985**, *14*, 245-260, and reference therein.
- [24] Hadjiivanov, K.I.; Klissurski, D.G. *Chem. Soc. Rev.* **1996**, *25*, 61-69.
- [25] Finnie, K.S.; Cassidy, D.J.; Bartlett, J.R.; Woolfrey, J. L. *Langmuir* **2001**, *17*, 816-820.

- [26] Hadjiivanov, K.I.; Davydov, A.A.; Klisurski, D.G. *Kinet. Catal. (Engl. version)* **1986**, *29*, 161-167.
- [27] Morterra, C. *J. Chem. Soc., Faraday I*, **1988**, *84*, 1617-1637, and reference therein.
- [28] Arrouvel, C.; Digne, M.; Breysse, M.; Toulhoat, H.; Raybaud, P. *J. Catal.* **2004**, *222*, 152-166.
- [29] Vittadini, A.; Selloni, A.; Rotzinger, F.P.; Graetzel, M. *Phys. Rev. Lett.* **1998**, *81*, 2954-2957.
- [30] Henderson, M. A. *Langmuir* **1996**, *12*, 5093-5098.
- [31] a) Gong, X.-Q.; Selloni, A.; Batzill M.; Diebold, U. *Nat. Mater.* **2006**, *5*, 665-670; b) Gong, X.-Q.; Selloni, A. *J. Catal.* **2007**, *249*, 134-139.
- [32] Martra, G. *Appl. Catal. A: General*, **2000**, *200*, 275-285.
- [33] Dzwigaj, S.; Arrouvel, C.; Breysse, M.; Geantet C.; Inoue, S.; Toulhoat, H.; Raybaud P. *J. Catal.*, **2005**, *23*, 6245-250.
- [34] Henrich, V. E.; Cox P. A. *The Surface Science of Metal Oxides*: Cambridge Univ. Press, Cambridge, 1994.
- [35] Freund, H. J. *Faraday Discuss.* **1999**, *114*, 1-31.
- [36] Cerrato, G.; Marchese, L.; Morterra, C. *Appl. Surf. Sci.* **1993**, *70/71*, 200-205.
- [37] Ohno, T.; Sarukawa, K.; Tokieda, K.; Matsumura, M. *J. Catal.* **2001**, *203*, 82-86.
- [38] Olivier, P.M.; Watson, G.W.; Kelsey, E.T.; Parker, S.C. *J. Mater. Chem.*, **1997**, *7*, 563-568.
- [39] Spoto, G.; Morterra, C.; Marchese, L.; Orio, L.; Zecchina, A. *Vacuum*, **1990**, *4*, 37-39.
- [40] Hadjiivanov, K.; Lamotte, J.; Lavalley, J.-C. *Langmuir* **1997**, *13*, 3374-3381
- [41] Hadjiivanov, K.I.; Vayssilov, G.N. *Adv. Catal.*, **2002**, *47*, 307-511.

[42] Marchese L., Boccuti M.R., Coluccia S., Lavagnino S., Zecchina A. In *Structure and Reactivity of Surfaces*; Morterra, C., Zecchina, A., Costa, G., Eds.; Elsevier, Amsterdam, 1989, p. 653-663.

[43] Eisenberg, D.; Kauzmann, W. *The structure and properties of water*: Oxford University Press, London, 1969.

[44] Barnard, A.S.; Zapol, P.; Curtiss, L.A. *Surf. Sci* **2005**, *582*, 173-188.

[45] Coluccia, S.; Lavagnino, S.; Marchese, L. *Mater. Chem. Phys.* **1988**, *18*, 445-464.

[46] Platero, E. E.; Scarano, D.; Spoto, G.; Zecchina, A. *Faraday Discuss. Chem. Soc* **1985**, *80*, 183-193.

[47] Hush, N. S.; Williams, M. L. *J. Mol. Spectrosc.* **1974**, *50*, 349-368.

[48] Lavalley, J.C. *Catal. Today* **1996**, *27*, 377-401.