Comparative visible-light driven selective oxidation to aldehydes of phenylmethanol (benzyl alcohol) and 4-pyridinylmethanol (4-pyridinecarbinol) on N-TiO₂ and some commercial TiO₂ samples

Luca Samiolo² · Rossano Amadelli² · Andrea Maldotti¹ · Alessandra Molinari¹

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Abstract

Visible light ($\lambda > 420$ nm) selective photooxidation of phenylmethanol and 4-pyridinylmethanol in CH₃CN to the corresponding aldehydes on N-TiO₂ is compared with homemade undoped TiO₂ (U-TiO₂) and commercial undoped anatase specimens (such as PC105, PC500). Significant differences observed between N-TiO₂ and undoped TiO₂ are neither directly related to the surface area nor to the adsorbed amount of alcohol in the dark by surface area unit. FTIR and EPR spectroscopies are used to study the surface of TiO₂ samples and to deeply understand the phenomena intervening in the visible-light photocatalytic activation of the doped vs the undoped oxides. In particular, it is shown that on N-TiO₂ (and also on undoped PC105) strong Lewis acid sites (LAS) exist. The favorable role of LAS on the photocatalytic activity is illustrated by the higher photooxidation of 4-pyridinylmethanol vs phenylmethanol over N-TiO₂ and PC105 in contrast to the other undoped samples, whose visible light sensitivity originates from a charge transfer between the alcohol and the solid. EPR spectra of N-TiO₂ point out the presence of paramagnetic centers related to nitrogen that disappear when the photocatalyst is irradiated with visible light in the presence of alcohol, which starts its oxidative process. On the basis of presented results, we propose that doping with N introduces new intraband gap states that not only contribute to LAS and adsorption of alcohol but also are directly involved in the photochemical process occurring under visible light irradiation.

Graphical abstract

Keywords N-doped TiO₂ · Benzyl alcohol · IR spectroscopy · Visible light · Lewis acid site

1 Introduction

A wide array of issues concerning photocatalysis by TiO₂ have been addressed, most notably its poor absorption of visible light. Accordingly, efforts to extend absorption into the visible spectral range have been important and research in this field has made significant progress (see for example Ref. [1]) while keeping in mind that high visible-light absorption alone does not necessarily imply a high photocatalytic activity. Several approaches have been explored including: (i) dye

✉ Alessandra Molinari
alessandra.molinari@unife.it

¹ Dipartimento di Scienze Chimiche, Farmaceutiche ed Agrarie, Università di Ferrara, Via L. Borsari 46, 44121 Ferrara, Italy

² c/o Dipartimento di Scienze Chimiche, Farmaceutiche ed Agrarie, ISOF CNR, UoS di Ferrara, Università di Ferrara, Via L. Borsari 46, 44121 Ferrara, Italy

sensitization [2], (ii) doping [3–11], and (iii) surface complexes formation [10, 12]. Some good results concerning the photocatalytic activity by visible light have been obtained with metal ion doping [3, 4]. Unsurprisingly, it was found that this activity depends on the preparation method: for example, in the case of Co-doped TiO_2 , surface interstitial doping was effective in the visible-light photocatalytic degradation of organic substrates, whereas lattice substitution was not [13].

Doping by non-metals, which was a relatively later strategy, has been a flourishing research field. Especially for nitrogen-doped TiO_2 (N- TiO_2), the number of publications and reviews has grown extensively [5–11].

Aside from the domain of photocatalysis, N-doped oxides have been successfully used for application in gate dielectric in field-effect transistors [14]. Concerning the location of the dopant, it is agreed that nitrogen can be incorporated in interstitial positions (N_i) and/or substitute for oxygen (N_s) but the debate on which of the two doping modes is more photochemically effective appears inconclusive.

Visible-light photocatalysis over N- TiO_2 [15–17] includes cases with significant activity [18] and others with no activity at all, also depending on the preparation method and on the target chemical compounds.

Quite a few studies have addressed the issue of selectivity, a key topic in fine chemicals production through photocatalysis and conventional catalysis [19]. In particular, the selective catalytic oxidation of alcohols to carbonyl compounds is one of the most important chemical transformations in organic syntheses also on an industrial scale [20]. In general, a selective reaction requires a surface arrangement that limits the reactivity of an adsorbed organic intermediate, so that desorption of partially oxidized species is faster than further oxidation.

Each step of the (photo)catalytic process must be optimized, and alcohol oxidation is, by the way, a typical reaction used to probe surface characteristics, such as, for example, vacancies and defects. The vast literature available on alcohols (photo)reactivity underlines that catalyst defects play a paramount role [21].

The photooxidation of phenylmethanol (benzyl alcohol; PhCH_2OH) to phenylmethanal (benzaldehyde; PhCHO) has often been investigated as a test reaction. In addition, benzaldehyde is widely used in a number of industrial processes as building block. In the research domain of surface electronics modification by adsorbed species and its effects on visible-light photocatalysis, a review containing key references focusing on the selective oxidation of benzyl alcohol derivatives has been published [10]. Both experimental data and theoretical calculations have indicated the appearance of new occupied and unoccupied states upon adsorption as a result of the hybridization of the PhCH_2OH molecular orbitals with the O_{2p} atomic orbitals of TiO_2 . Charge transfer

(CT) complexes are thus formed, giving rise to visible-light response [10].

In a study on the selective conversion of benzyl and cinnamyl alcohols to the corresponding aldehydes [22], it was observed that on a homemade N- TiO_2 the photocatalytic process was totally selective. Conversely, Li et al. [23] reported that the photocatalytic activity of N- TiO_2 for benzyl alcohols oxidation was very poor. This discrepancy furtherly confirmed the effect of the preparation methods on the visible-light photocatalytic activity of these materials.

In this broad context, the present work examines the visible-light photooxidation of PhCH_2OH to PhCHO on N- TiO_2 in comparison with that obtained on homemade undoped TiO_2 (U- TiO_2) and some commercial undoped anatase specimens, such as PC105 and PC500. The focus was photocatalytic process selectivity while also seeking additional elements that could increase our understanding of the phenomena intervening in the visible-light photocatalytic activity of the doped vs the undoped TiO_2 . In particular, the importance of Lewis acid sites (LAS) that can favour adsorption of alcohols behaving as Lewis bases is highlighted here. In fact, the role of LAS, related to surface coordinative unsaturation, has been often stressed as an important property affecting surface reactivity at metal oxides and continues to be an interesting topic of research [24–26]. In particular, their role in photocatalytic reactions, including the oxidation of benzyl alcohols, has recently been discussed [27, 28].

To our knowledge, Lewis surface acidity of N- TiO_2 prepared by the wet method, has not been examined before. The comparative investigation on N- TiO_2 and on several TiO_2 samples reported here benefits not only from FTIR studies of acetonitrile or pyridine adsorption, but also from the results of 4-pyridinylmethanol (PyCH_2OH) selective photooxidation to the corresponding aldehyde (PyCHO), compared to that of PhCH_2OH . In addition, using room temperature EPR spectroscopy, we highlight differences in the mechanism of selective PhCH_2OH photooxidation on N- TiO_2 , in contrast with unmodified commercial anatase samples, which only involve a photochemical CT process induced by adsorption.

2 Experimental

2.1 Materials

All chemicals, viz. acetonitrile (<0.005% water), anhydrous PhCH_2OH , PyCH_2OH , PhCHO and PyCHO were obtained from Sigma-Aldrich and used as received.

Homemade nitrogen-doped and undoped TiO_2 were obtained following a previously reported procedure [22], which involves precipitation from TiOSO_4 with NH_4OH (N- TiO_2) or NaOH (U- TiO_2). The TiO_2 (anatase) samples

PC500 and PC105 were Cristal Millenium products (the latter obtained from the first by a sintering process) and have previously been characterized (see, for example, Ref. [29]). Following evacuation at 120 °C, the TiO₂ samples were stored in a dry atmosphere under argon.

2.2 Equipment

In adsorption and photocatalytic experiments, the chemical analyses were carried out on a HP6890 gas chromatograph (Agilent Technologies) equipped with a flame ionization detector using an HP-WAX capillary column for PhCH₂OH and a DB624 capillary column for PyCH₂OH. For quantitative analysis, we constructed calibration curves using the pure alcohols or the corresponding aldehydes at different concentrations. In addition, the conversion of PyCH₂OH to PyCHO was followed also by UV visible spectroscopy (Jasco V570). The irradiation source was a Hg medium pressure lamp (Helios Italquartz) equipped with cutoff filters. Monochromatic filters were used for the calculation of quantum yields.

A FTIR Bruker Vertex 70 spectrometer equipped with a CricketTM accessory was used to record diffuse reflectance FTIR (DRIFT) spectra at 1 cm⁻¹ resolution. All DRIFT measurements were performed at room temperature and results are reported as absorbance spectra.

EPR experiments were carried out at room temperature using a X band Bruker 220 SE spectrometer. Flat quartz cells were employed for powder suspensions. MW Frequency 9.4 GHz, MW power 63mW, Mod. Amplitude 100 kHz. The instrument was calibrated with 1,1-diphenyl-2-picrylhydrazyl (DPPH; *g* value: 2.0036) as reference. In some cases, the samples placed in the instrument cavity were directly exposed to the light emitted by the aforementioned Hg medium pressure lamp equipped with a $\lambda > 420$ nm cutoff filter.

DR–UV–Vis spectra were collected with a Jasco V-570 spectrophotometer equipped with a diffuse reflectance accessory and using BaSO₄ as reference.

2.3 Methods

The amount of adsorbed alcohol (q_{ads}) was obtained by suspending the photocatalyst (4 g L⁻¹) in a CH₃CN solution of the alcohol (1×10^{-3} M) and stirring this suspension in the dark for 1 h. The results reported are the average of at least five repeated experiments. In this case as well as in all other experiments, final results were accepted with an error lower than 5%.

All DRIFT spectra were recorded against air on powders that were mixed in fixed proportion with KBr. For the

spectra of modified TiO₂, the dry powder of the samples were exposed to vapours of either acetonitrile or pyridine in a controlled stream of dry argon followed by evacuation at 100 °C. In each case a baseline was recorded using the same, unmodified TiO₂; the instrument allows an automatic background correction. Reproducibility was checked by comparing spectra recorded in the same conditions.

Photocatalytic experiments were conducted with suspensions composed as described just above. A small Pyrex semi-cylindrical reactor with a flat window was used. The suspension was magnetically stirred, oxygenated by maintaining the reactor under pure O₂ at 1 atm, and irradiated (1 h) with the aforementioned medium pressure Hg lamp equipped with cutoff or monochromatic filters. No oxidation products were obtained when the experiments were run in the dark or when the oxygenated alcohol solutions were irradiated in the absence of a photocatalyst.

Evaluation of quantum yields (Eq. 1) was done with monochromatic irradiation, using a fixed amount (4 g L⁻¹) of photocatalyst and the measured initial rates of aldehyde formation that were normalized to the surface areas of the photocatalyst employed [22]:

$$\varphi = \frac{\text{rate of RCHO formation} (\mu\text{mol m}^{-2} \text{s}^{-1})}{\text{photon irradiance} (\mu\text{mol m}^{-2} \text{s}^{-1})} \quad (1)$$

The incident light intensity ($\mu\text{W cm}^{-2}$) was measured with a power meter Newport Mod. 1918-C. The photon irradiance refers to the net light intensity measured across the cell in the absence and in the presence of the suspension; in all cases the amount of the suspension ensured complete absorption of the incident light.

3 Results and discussion

The photocatalytic activity is examined for visible light irradiation only, since, as mentioned earlier [22], in the UV-region undoped and N-doped TiO₂ behave similarly, i.e., a relatively high reactivity but a low selectivity toward aldehyde formation.

Section 3.1 concerns the dark adsorption and selective photocatalytic oxidation of PhCH₂OH. Section 3.2 focuses on the role of LAS in the adsorption process, because, as anticipated in the Introduction, the adsorption of alcohols on metal oxides is often related to LAS. Section 3.3 continues the analysis of the role of LAS by reporting results on the dark adsorption and the photocatalytic oxidation of PyCH₂OH, which is a more basic substrate than PhCH₂OH. Finally, Sect. 3.4 reports room-temperature EPR measurements regarding N-TiO₂ on the presence of nitrogen impurities and defects associated with LAS.

3.1 Photocatalytic oxidation of phenylmethanol (PhCH₂OH)

Table 1 reports the adsorbed amounts in the dark per surface area unit (q_{ads}) and the visible-light selective conversion of the alcohol to the corresponding aldehyde (PhCHO/PhCH₂OH ratio) on laboratory prepared doped (N-TiO₂) and undoped (U-TiO₂) catalysts as well as on some anatase commercial samples; for completeness surface areas and average particle sizes are also listed.

It appears that under prolonged irradiation (1 h) the formation of PhCHO on commercial catalysts roughly increases with increasing surface area and hence, possibly, with the number of OH groups [30]. One can also identify a correlation between q_{ads} and PhCHO formation. Most importantly, this table shows the substantial effect of nitrogen doping on this oxidation under visible-light irradiation. This effect appears especially evident when comparing N-TiO₂ with U-TiO₂ and PC105 whose surface areas and q_{ads} values are close.

The high conversion (PhCHO/PhCH₂OH = 0.98) obtained with N-TiO₂ is in accordance with the visible light absorption of this sample beyond 400 nm (Fig. 1S, curve 1). Figure 1S reports also the UV–visible spectrum of PC500 (curve 2): as expected, when PhCH₂OH is present, surface adsorption on TiO₂ occurs (Fig. 1S, curve 3), giving rise to a ligand-to-metal charge transfer band (LMCT) in the visible spectral region [10]. A comparison between curves 1 and 3 shows that LMCT absorption was weaker than that observed with N-TiO₂ by a factor of 4–5.

The activity of a catalyst, in general, can be affected by factors related to the extension of the surface area and/

or by the presence of active sites [31]. In general, it is not always a question of the number of sites but also of their nature. The full identification of active sites on surfaces is a challenging task, and the following text includes results regarding the nature of active sites that could be involved in our probe photocatalytic process.

3.2 DRIFT spectra of adsorbed CH₃CN and pyridine

3.2.1 CH₃CN

In the present study, acetonitrile was used as the solvent; calculations have shown that it forms a strongly oriented layer at the TiO₂ interphase [32]. In the case of N-TiO₂, some of us have pointed out an important role in photoelectrocatalysis of the interaction of CH₃CN with the surface [22].

It is also noteworthy that acetonitrile is a medium strength base that has frequently been employed to assess the presence of acidic surface sites of oxides, including TiO₂. Its interaction with Brønsted (–OH...N≡C–CH₃) and with Lewis acid (–Ti...N≡C–CH₃) surface sites has been conveniently investigated by FTIR spectroscopy [33–39]. Thus we employed this technique with the aim to gain a first insight into the characteristics of N-TiO₂ compared with undoped U-TiO₂ and with commercial TiO₂.

Figure 2S displays the OH stretching region before and after contact of N-TiO₂ with CH₃CN. The spectrum obtained in the absence of CH₃CN shows narrow bands in the 3600–3800 cm^{−1} region which are assigned to differently coordinated surface OH groups [35]. As observed before [36], exposure to CH₃CN caused a pronounced intensity decrease of the bands at 3665 and 3695 cm^{−1} attributed to Brønsted acidity.

More interestingly, Fig. 1 shows bands at lower wavenumbers with both PC500 and U-TiO₂ (part A) and with N-TiO₂ (part B) after the contact with CH₃CN. In Fig. 1A, the bands at 2320 and 2292 cm^{−1} match the reported values for the C≡N stretching of CH₃CN adsorbed on Lewis acid sites (LAS) of anatase via the nitrogen lone pair [38–40]. In the same spectral region, the broad band at 2350 cm^{−1} observed for N-TiO₂ (Fig. 1B) is suggested to correspond to the Ti...NCCH₃ interaction, already observed for the undoped oxide, but shifted to higher wavenumbers, indicating the existence of stronger LAS [40].

Among the commercial TiO₂ samples, PC105 represents a particular case: in addition to bands at 2320 and 2292 cm^{−1} as for PC500 (Fig. 1A), it shows a band at 2340 cm^{−1} and a pronounced shoulder at 2323 cm^{−1} (Fig. 2). These higher wavenumber signals can be ascribed to the presence of LAS in the commercial PC105 too.

Table 1 Adsorbed amount and visible light photocatalytic conversion of benzyl alcohol (PhCH₂OH) to benzaldehyde (PhCHO) on nitrogen-doped TiO₂ (N-TiO₂), undoped home-made TiO₂ (U-TiO₂) and on commercial TiO₂ specimen

TiO ₂ sample	BET area (m ² g ^{−1}) ^a	Average particle size (nm)	PhCH ₂ OH adsorbed (q_{ads} , μmol m ^{−2}) ^b	PhCHO/PhCH ₂ OH ^b
N-TiO ₂	80	22	0.14	0.98
U-TiO ₂	75	20	0.11	0.13
PC105	85–95	20	0.10	0.19
PC500	317	8	0.16	0.28

^aThis paper and Ref. [29]

^bComparative experiments were carried out suspending a fixed amount of catalyst (4 g L^{−1}) in a CH₃CN solution containing PhCH₂OH (1 × 10^{−3} M) followed by visible light irradiation (λ > 420 nm). Adsorption in the dark and the effects of illumination were evaluated after 1 h equilibration. Quantitative analyses were carried out by gas chromatography (see Experimental section). Reported results are the average of several repeated experiments. Errors never exceeded ± 5%

Fig. 1 DRIFT spectra in the CN stretching region for CH₃CN adsorbed on PC500 and U-TiO₂ (A) and on N-TiO₂ (B)

Fig. 2 DRIFT spectra in the CN stretching region for CH₃CN adsorbed on PC105

3.2.2 Pyridine

To confirm the presence of Lewis/Brønsted acid sites we used pyridine, which has been widely employed as an IR probe to reveal the presence of acid sites on surfaces [41], including TiO₂ [42]. FTIR spectra for pyridine adsorbed on different TiO₂ samples are given in Fig. 3. It is seen that the presence of LAS on N-TiO₂ is important (trace 1). On the contrary, PC500 shows a comparatively low surface Lewis acidity (trace 3); a very similar behavior is observable for U-TiO₂ (data not shown). Interestingly, the behaviour of PC105 is again intermediate (trace 2).

It is sometimes stated that DRIFT measurements can reveal trends although they do not allow precise acid site quantification [43]. In principle, however, the knowledge of integrated areas of the band at 1445 cm⁻¹ (Fig. 3) and of

Fig. 3 DRIFT spectra of adsorbed pyridine on different TiO₂ samples: 1 N-TiO₂, 2 PC105, 3 PC500. (L stands for Lewis and B for Brønsted)

the surface concentration of the probe (μmol m⁻²) (Fig. 3S) allows an estimation of the number of LAS [44]. Since a comparison seems to be more rigorous for samples having similar areas and particle sizes [45], our focus was restricted to N-TiO₂ and PC105 among commercial samples (Table 1); the results (Supplementary Information) showed that the proportion of LAS on N-TiO₂ is higher than that of PC105 by a factor of about 2.

Several reasons can be mentioned for the higher density and strength of LAS of PC105 than of PC500 (Fig. 3S). Possibly, during the sintering of PC500 to prepare PC105 some planes could be preferentially exposed. Changes in LAS due to differences in the geometric arrangement of the surface O²⁻ anions could hence occur, which seemingly indicates that the chemical behaviour of both Lewis acid and Lewis base sites depends on the surface structure. In this regard, an important recent FTIR study by Mino et al. [46] shows, for the particular case of PC105, the contribution of facets and Ti centres with high coordinative unsaturation (and high Lewis acidity).

Alcohols are weak Lewis bases and, in principle, their adsorption is expected to be stronger at LAS. From a general point of view, a possible pathway of alcohol adsorption would be dissociation at defects [47]:

where V_o is an oxygen vacancy, O_b is a bridge oxygen and Ti_{5c} are coordinatively unsaturated Ti cations. Because of their unsaturated coordination, both V_o and Ti_{5c} are Lewis acidic sites [21, 47].

We note, however, that the difference in LAS between PC105 and PC500 (vide supra) did not affect the dark

adsorption and the photocatalytic oxidation of PhCH₂OH (Table 1), as one would expect from reactions 2 and 3. The reason may be that PC105, as the other undoped TiO₂ samples, likely follows the mechanism proposed by Higashimoto [10], whereby benzyl alcohol molecules first interact with surface OH groups and then rearrange to form a surface complex [21, 48].

Recent calculations reveal that the first step is the determining one, since the intermolecular dehydrogenation is a fast step, possessing very low or almost zero barrier [49]. We can speculate that despite clear evidence of Lewis acid sites on PC105, these are not sufficiently strong to change the adsorption mechanism of a weak base as benzyl alcohol.

Concerning N-TiO₂, the comparison with and without adsorbed PhCH₂OH, gives a difference FTIR spectrum that shows negative bands between 3100 and 3700 cm⁻¹ (Fig. 4S), confirming that this alcohol interacts with the surface OH groups as reported in earlier works. It is noteworthy that this difference spectrum also contains a new positive band at ~1100 cm⁻¹ that is generally attributed to alcohols adsorbed in the form of alcoholate [33, 50]. For PhCH₂OH this band is clearly visible only in the case of N-TiO₂ and one is tempted to attribute the high photoactivity of this catalyst to a more favourable alcoholate formation due to the presence of stronger LAS on this catalyst.

To get more insights into the factors governing the mechanisms, in the following we will consider the effect of the alcohol nature on adsorption, reactivity and selectivity.

3.3 DRIFT spectra and photocatalytic oxidation of 4-pyridinylmethanol (PyCH₂OH)

The characterization of surfaces with probe molecules that are also reactants is more appropriate if the goal is to investigate on the possible influence of acidic or basic properties on the photocatalytic activity [51]. The cases of benzyl alcohol and benzyl amine [52] might provide an example. We then decided to complement the results of Sect. 3.2 with those obtained using PyCH₂OH as the starting substrate; this compound appeared to be a good candidate, because the lone electron pair of the N atom is expected to interact with LAS.

3.3.1 DRIFT spectra

Comparison of the data in Tables 1 and 2 shows that the amount of PyCH₂OH adsorbed, for example, on PC105 and N-TiO₂, is higher by a factor of about 12 in comparison to analogous data for PhCH₂OH. The presence of different functionalities in this molecule causes the alcohol molecule to bind with several surface centres simultaneously [33].

This higher adsorption is in line with the presence of stronger LAS as determined from the FTIR spectra of adsorbed acetonitrile and pyridine (see previous Section).

Table 2 Adsorbed amount and visible light photocatalytic conversion of 4-pyridinylmethanol (PyCH₂OH) to the corresponding aldehyde (PyCHO) on nitrogen-doped TiO₂ (N-TiO₂), undoped home-made TiO₂ (U-TiO₂) and on commercial TiO₂ specimen

TiO ₂ sample	BET area (m ² g ⁻¹) ^a	PyCH ₂ OH adsorbed (<i>q</i> _{ads} , μmol m ⁻²) ^b	PyCHO/PyCH ₂ OH ^b
N-TiO ₂	80	1.62	0.80
U-TiO ₂	75	0.43	0.18
PC105	85–95	1.20	0.56
PC500	317	0.61	0.20

^aThis paper and Ref. [29]

^bComparative experiments were carried out suspending a fixed amount of catalyst (4 g L⁻¹) in a CH₃CN solution containing PyCH₂OH (1 × 10⁻³ M) followed by visible light irradiation (λ > 420 nm). Adsorption in the dark and the effects of illumination were evaluated after a 1 h experiment. Quantitative analyses were carried out by gas chromatography (see Experimental Section). Reported values are the average of several repeated experiments. Errors never exceeded ± 5%

Indeed, the FTIR spectra of PyCH₂OH adsorbed on N-TiO₂ or PC105 (Fig. 5S) presented a new band at 1445 cm⁻¹ typical of the interaction of the pyridine moiety of PyCH₂OH with LAS. In addition, the FTIR spectra of PyCH₂OH adsorbed on both N-TiO₂ and PC105 featured a band at ~1178 cm⁻¹ (Fig. 5S). This band is assigned to the C–O stretching mode of an adsorbed alcoholate and provides evidence of the stronger interaction of PyCH₂OH with these two samples, in agreement with what reported above.

3.3.2 Photocatalytic oxidation of PyCH₂OH

Table 2 reports data concerning the formation of the aldehyde (PyCHO) under prolonged irradiation. In addition, for both the alcohols considered, PhCH₂OH and PyCH₂OH, we evaluated reactivity as initial rates of aldehyde formation (*r*^o) and quantum yields to minimize possible effects of alcohol–aldehyde adsorption competition (Table 3). An examination of *r*^o versus *q*_{ads} clearly reveals that, for the particular case of PC105, there is a striking photoactivity change upon changing the reactant alcohol.

As mentioned above, the results for PhCH₂OH show that there is no apparent correlation between LAS and the photocatalytic activity of all the non-doped TiO₂ samples investigated (Tables 1 and 3). In these cases, the TiO₂ activity approximately increases with increasing surface area, both under steady-state and initial conditions. This seemingly confirms the mechanism proposed in the works by Higashimoto [10].

Conversely, the high reactivity of PyCH₂OH on PC105 (Tables 2 and 3) cannot be explained by area effects. Since the number of LAS actually made available depends, among other factors, on the nature of the molecule to

Table 3 Initial rates of aldehyde formation from PhCH₂OH or PyCH₂OH and corresponding quantum yields for N-TiO₂ and various TiO₂ samples under irradiation at 404–407 nm

Sample	PhCH ₂ OH			PyCH ₂ OH		
	$r^{\circ a}$	q_{ads}^b	φ^c	$r^{\circ a}$	q_{ads}^b	φ^c
N-TiO ₂	8.3×10^{-2}	0.14	1.70×10^{-2}	0.73	1.62	0.150
U-TiO ₂	7.2×10^{-3}	0.11	1.45×10^{-3}	0.27	0.43	0.032
PC105	8.0×10^{-3}	0.10	1.63×10^{-3}	0.65	1.20	0.130
PC500	1.4×10^{-2}	0.16	2.80×10^{-3}	0.38	0.61	0.080

^a r° = initial rates ($\mu\text{mol m}^{-2} \text{s}^{-1}$)^b q_{ads} = amount of adsorbed alcohol ($\mu\text{mol m}^{-2}$) (Tables 1, 2)^c φ° = quantum yield using initial rates (see Eq. 1). Initial rates were determined by gas chromatography (see Experimental section)

be adsorbed [40], we conclude that the reactivity of PyCH₂OH on PC105 is related to the reactant basicity that favours its interaction with LAS that are present in higher amount on this particular catalyst in comparison with the other undoped samples.

Peculiar characteristics of the surface/interface must, likewise, be the base of the high photocatalytic activity of N-TiO₂ in the selective oxidation of both PhCH₂OH and PyCH₂OH; area effects and the number and strength of LAS alone are not sufficient to explain the behaviour of this catalyst. The nitrogen dopant introduces intra-bandgap energy levels and surface modifications [53] that are the possible reason of the Lewis acidity increase. In principle, we can envisage a specific interaction of alcohols with the dopant levels leading to a different oxidation mechanism on N-TiO₂ compared with that on undoped TiO₂ samples.

In regard to N-TiO₂ selectivity, note that the PyCHO/PyCH₂OH ratio decreases with respect to analogous results obtained with PhCH₂OH (cfr. Tables 1 and 2), which might be surprising in view of r° and quantum yield parameters shown in Table 3. Under prolonged irradiation, it can be explained by a strong interaction of PyCHO with the surface that leads to a slow desorption, in turn, reasonably leading to its further transformation rather than accumulation.

Inspection of the FTIR spectrum for N-TiO₂/PyCH₂OH (Fig. 5S curve b) reveals a band at $\sim 1730 \text{ cm}^{-1}$ that is attributed to the C=O stretching mode of PyCHO. In the absence of irradiation it is seemingly formed upon absorption of ambient light. To check that, we exposed a stirred suspension of N-TiO₂ in CH₃CN containing PyCH₂OH ($1 \times 10^{-3} \text{ M}$) to laboratory ambient light and found that 78% of the initial PyCH₂OH was converted selectively to PyCHO in 150 min (Fig. 6S). The reason why this system is so sensitive to visible light is assumed to be related to the interaction of both the pyridinyl nitrogen atom and the –CH₂OH functional group with the surface. This increased interaction is favoured by the high amount of strong LAS on N-TiO₂ and on PC105, resulting in an increase of the concentration of surface species. The EPR investigation reported in the following section provides evidence for this interaction.

3.4 Electron Paramagnetic Resonance Spectroscopy (EPR)

EPR spectra could be observed at room temperature only for N-TiO₂ (Fig. 4A, curve a) and not for any of the other undoped TiO₂ samples. This particular spectrum is similar

Fig. 4 **A** Room temperature EPR spectra of deaerated N-TiO₂ suspended in CH₃CN in the dark (curve a, dotted line) and after irradiation ($\lambda > 420$) for 5 min (curve b, solid line). **B** Net EPR spectra (light–dark) in the absence (1) and in presence (2) of PhCH₂OH (2 mmol L⁻¹ in CH₃CN). The asterisks denote the triplet ascribed to paramagnetic nitrogen in N-TiO₂ (see text)

Scheme 1 Simplified illustration of the processes that we suggest may occur on N-TiO₂ in CH₃CN/RCH₂OH under visible-light irradiation.

to those reported before at low temperature and discussed in previous literature [18, 54, 55]. However, broad the signal is, it is possible to observe a larger peak at $g = 2.0045$ and weaker peaks at $g = 2.022$ and $g = 1.985$, each at a distance of 32 G from the main one. This often-reported EPR triplet is seemingly a feature of nitrogen impurities in TiO₂ [1, 11, 18], and corresponds to a paramagnetic species $N_i^\bullet$ from interstitial nitrogen (N_i) chemically bound to a lattice [11, 56]. The N_i localized energy state is located a few tenths of eV above the valence band [57] and is identified as the active centre of visible light photoactivity. Feng et al. [54, 55] described the active centre as $V_o^\bullet\text{-NO-Ti}$ to underline a role of vacancies [56, 57].

Under irradiation with visible light ($\lambda > 420$ nm) of deaerated N-TiO₂ suspensions, the intensity of the EPR signal increases (Fig. 4A, curve b), as often reported (for example Refs. [55, 56, 58]). In particular, irradiation causes a significant increase in the formation of paramagnetic $N_i^\bullet$ as clearly evident in the net spectrum (light–dark) of Fig. 4B (curve 1). This behaviour is attributed to visible-light excitation of electrons from the occupied N_i bandgap level to the conduction band [58].

For analogous experiments in the presence of PhCH₂OH as the oxidizable species (Fig. 4B, curve 2), the net spectrum shows no evidence of $N_i^\bullet$ formation. This is apparently due to charge transfer from the adsorbed alcohol to holes created in the N_i band gap level by visible-light irradiation (reaction 4). This, indeed, can explain the disappearance of the paramagnetic nitrogen centres and formation of an activated adsorbate (reaction 5). Overall, the process can then be written as:

At the same time, the broad signal with $g \approx 1.99$ is not identified with firm certainty but falls in the range of g values assigned to Ti^{3+} (trapped electrons) [55, 59, 60], seemingly indicating that, following reactions (3–4) in anaerobic conditions, accumulation of electrons occurs (Scheme 1).

In addition, the shoulder (at $g = 2.010$), observed only in the presence of the alcohol (Fig. 4B, curve 2), might be tentatively explained by the formation of surface-stabilized alkoxy ($\text{PhCH}_2\text{O}^\bullet$) radicals [61, 62]. Kindly check Graphical abstract and Scheme 1 are identified correctly, as the images seems to be same. Scheme 1 is correct. The correct Graphical Abstract has been attached.

To sum up, we think that the EPR data provide important new evidence on the mechanism of photochemical processes occurring on N-TiO₂ under visible-light irradiation. In the context of this predominant reaction mechanism, the role of the strong LAS on the surface of this catalyst would be to contribute to increase the concentration of the reacting species.

4 Conclusions

The selective oxidation of two structurally related alcohols, PhCH₂OH and PyCH₂OH, to the corresponding aldehydes under visible-light irradiation, occurs with different efficiency and via different mechanisms on a home-prepared N-TiO₂ and on commercial undoped TiO₂ samples.

FTIR spectra of adsorbed acetonitrile and pyridine have shown the presence of strong Lewis acid sites (LAS) on N-TiO₂ and on one of the undoped commercial samples (PC105). Nevertheless, the selective oxidation of PhCH₂OH on all commercial materials does not depend on Lewis acidity but rather correlates with surface area. This correlation is consistent with a mechanism involving the adsorption of PhCH₂OH on the surface and its interaction with OH surface groups leading to the formation of CT complexes between the alcohol and TiO₂. The photoactivity of N-TiO₂ is comparatively higher and does not obey this trend.

In the oxidation of PyCH₂OH, the photoactivity of PC105 becomes close to that of N-TiO₂. This drastic change of reactivity compared to the analogous case of PhCH₂OH can likely be ascribed to a contribution of strong LAS that respond to the Lewis basicity of this molecule.

Room temperature EPR investigations performed with N-TiO₂ suggests that nitrogen doping is responsible of intra band gap levels. Visible-light irradiation starts a new oxidation mechanism that involves a charge transfer from the adsorbed alcohol to holes photogenerated in the nitrogen dopant band gap level. As the amount of adsorbed reactant matters, the strong LAS of this catalyst plausibly increase the alcohol concentration on the surface.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s43630-021-00137-4>.

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Declarations

Conflict of interest There are no conflicts to declare.

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