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ESR study of the initial stages of the photocatalytic oxidation of toluene over TiO_2 powders

Juan M. Coronado [a,*], Javier Soria [b]

[a] *Environmental Applications of Solar Radiation, CIEMAT, Avenida Complutense, 22, building 42, 28040 Madrid, Spain*
[b] *Instituto de Catálisis y Petroleoquímica, CSIC, c/Marie Curie, 2, Cantoblanco, 28049 Madrid, Spain*

Abstract

In the present work, the initial stages of the photocatalytic oxidation of toluene over two commercial TiO_2 powders were investigated at the molecular level by ESR spectroscopy. UV-irradiation of the TiO_2 samples, which present different phase composition and surface area, gave rise to several oxygenated radicals like $O^{\bullet -}$, $O_2^{\bullet -}$ and $O_3^{\bullet -}$, as well as Ti^{3+} centers. The proportion of these species generated depends on the gaseous environment (vacuum or oxygen), and the structural and morphological characteristic of the TiO_2 samples. In contrast, co-adsorption of toluene and oxygen on any of the TiO_2 samples studied yields upon UV illumination slightly different ESR signals, which have been assigned to the formation of benzylperoxy radicals, Ph-$CH_2OO^{\bullet}$, adsorbed on the semiconductor. Such species are only detected when TiO_2 is exposed to toluene–oxygen mixtures enriched in the organic, and under these conditions neither of the other oxygenated radicals is formed. The reasons for this behavior are discussed on the basis of the mechanism for the photocatalytic oxidation of toluene.

Keywords: Photocatalysis; TiO_2; ESR; Toluene; Peroxy; Radicals; Reaction mechanisms

1. Introduction

The mechanism of many catalytic processes implies electron exchange between adsorbed molecules and the solid surface. Among others, well-known examples are catalysts for fuel-cells electrodes and three-way converters [1,2]. Consequently the study of electronic flow through the gas–solid or liquid–solid interface is crucial for understanding catalytic redox reactions [2,3]. Nevertheless, relatively few studies have been devoted to investigate the electric properties of catalyst and their correlation with activity [2,4–6]. In this respect, methods based on microwave absorption, like microwave Hall effect (MHE), have successfully used for determining both electrical mobility and conductivity of catalyst exposed to different gaseous environments [5,6]. Similarly, electron spin resonance (ESR) is a suitable technique for monitoring redox surface reactions, because this spectroscopy can detect many adsorbed intermediates originating from electron transfer [3,4,6].

ESR spectroscopy has been frequently applied to investigate the initial steps of photocatalytic reactions at a molecular level. In particular, this technique has been used for following the photoinduced generation of charge carriers on TiO_2 and its transfer to inorganic adsorbed molecules like O_2 and H_2O [7–10]. In contrast, ESR investigation of organic radicals formed upon UV-illumination of TiO_2 has received less attention, despite the fact that they could provide relevant insight into the mechanisms of pollutant photooxidation. The main reason for lack of studies is that reactive organic intermediates are frequently unstable and consequently their detection is challenging [11–13]. In this respect, hydroxymethyl radicals, $CH_2OH^{\bullet}$, are observed only when a methanol solution is irradiated in the presence of precious metal loaded TiO_2, but they cannot be detected when pure TiO_2 suspensions are employed [11]. Adsorbed alkylperoxide radicals, R-$OO^{\bullet}$, are identified on the TiO_2 surface when exposed to mixtures of acetone and oxygen with high organic to oxygen ratio, and subsequently irradiated at low temperature [12]. Similarly, peroxyacyl species, $RCO_3^{\bullet}$, are formed upon UV irradiation of aldehydes and oxygen coadsorbed on rutile titania [13].

In the present work, we investigate by ESR the photocatalytic oxidation of toluene over commercial TiO_2 powders

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* Corresponding author. Tel.: +34 91 3466177; fax: +34 91 3466037.
E-mail address: juanmanuel.coronado@ciemat.es (J.M. Coronado).

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with different phase composition and surface area. Toluene is a widespread pollutant whose removal is high priority, but its photocatalytic degradation can be hindered by severe TiO_2 deactivation. This process has been related to the progressive accumulation of partially oxidised intermediates on the semiconductor surface [14,15]. Therefore, a better understanding of the mechanism at molecular level may contribute to the design of more efficient photocatalysts.

2. Experimental

Two commercial TiO_2 samples were used in this study: (i) Degussa P25, which constitutes a standard photocatalyst, and it is composed by approximately 80% anatase and 20% rutile, with a BET surface area of 45 $m^2\,g^{-1}$; (ii) Brunschwig Chemie (BDH), 100% anatase, with a surface area of 10 $m^2\,g^{-1}$.

ESR measurements were carried out with a Bruker ER200D instrument operating in the X-band. Aliquots of the catalyst were placed into a special cell made of spectroscopically pure quartz and provided with greaseless stopcocks. Approximately the same volume of each catalyst was used to maintain a homogeneous illumination of the powders. However, due to the large differences in the apparent density of each TiO_2 samples, the mass employed was about 3 mg for P25 and 30 mg for BDH. For outgassing treatments and gas adsorption the cell was attached to a conventional vacuum manifold, which achieves pressures down to 10^{-4} N m^{-2}. All the spectra were recorded at 77 K in a double T type cavity. The frequency of the microwave was calibrated for each experiment using a standard of diphenyl-picryl-hydrazyl (DPPH) located in the second cavity, which shows an intense symmetric signal at $g = 2.0036$. Irradiation treatments were carried out for 15 min at 77 K by placing the cell in a quartz Dewar flask filled with liquid N_2. This low temperature of operation is crucial for increasing the sensitivity and stabilising labile species. For these experiments four fluorescent lamps (Sylvania, 6WBLB-T5, 6 W, maximum emission at 365 nm) were used as UV source.

Toluene (Aldrich, HPLC grade) was outgassed in vacuum using several freeze-thaw cycles before use to eliminate dissolved air. Oxygen (L'air Liquide) used in the experiments was purified using cold trap in order to remove traces of moisture. Doses of about 3 μmol mg^{-1} were used for the oxygen and toluene adsorption experiments, although in the case of oxygen adsorption extensive evacuation was performed to increase the ESR sensitivity. Therefore, the final toluene to oxygen molar ratio adsorbed in the TiO_2 is estimated to be larger than 5.

In a typical experiment the TiO_2 sample was first evacuated at room temperature for 1 h, in order to obtain a hydroxylated surface free of other weakly adsorbed molecules, and then UV-irradiated at 77 K to produce photogenerated species. Subsequently, an oxygen dose was admitted in the cell at the same temperature. Further irradiation in the presence of adsorbed oxygen can enhance the spectrum intensity due to the ability of this molecule to trap photogenerated electrons. However, if oxygen is in excess, surface radicals vanish due to dipole interactions with O_2. Therefore, an additional outgassing treatment at 77 K is usually necessary to enhance detection. Afterwards, a dose of toluene was introduced to determine any possible interaction with the photogenerated radicals. Following this, a short room temperature treatment was carried out to gain information about the thermal stability of the detected species, and to allow a more uniform distribution of the adsorbed molecules on the TiO_2 surface. Finally, the cell was again UV-illuminated at 77 K with O_2 and toluene co-adsorbed to study the initial steps of the photocatalytic reaction.

3. Results

In order to obtain a clean surface the TiO_2 P25 sample was treated at 573 K in air and subsequently outgassed briefly at room temperature (RT) to remove oxygen. Under these conditions the ESR spectra of the sample shows a symmetric signal, labelled A, at $g = 2.004$, which is relatively narrow ($\Delta H_{pp} \sim 5$ Gauss), as it can be observed in Fig. 1a. Similar signals has been previously assigned to electron trapped in oxygen vacancies, $V_O{}^+$, which are formed on TiO_2 and other materials like ZnO [3,6]. Subsequent UV irradiation at 77 K, generates two new signals (see Fig. 1b), one orthorhombic with components at $g_1 = 2.029$, $g_2 = 2.016$, and $g_3 = 2.003$, denoted as O1, and another signal with a single feature at $g = 1.991$, is labelled T1. This high field feature can be ascribed to the $g_\perp$ component of an axial signal characteristic of Ti^{3+} centers on anatase [8,10]. On the other hand, signal O1 is related to the presence of $O^{\bullet-}$ radicals formed upon irradiation in accordance with previous reports [8–10,16]. The g components of these signals along with their assignment are summarised in Table 1.

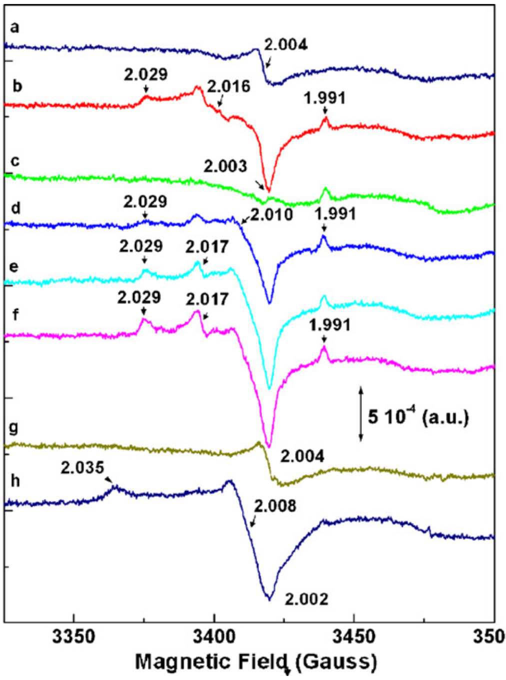

Fig. 1. EPR spectra at 77 K of (a) TiO_2 P25 calcined at 573 K and outgassed at RT, (b) UV-irradiated, (c) exposed to an excess of oxygen, (d) outgassed at 77 K for 30 min, (e) contacted with toluene at 77 K, (f) UV-irradiated, (g) warmed to RT, and (h) UV-illuminated again at 77 K.

Table 1
ESR parameters and assignment of photogenerated radicals detected on the different TiO_2 samples (see text for details)

Signal	ESR parameters	Assignment
A	$g = 2.004$	V_O^+
O1	$g_1 = 2.029$, $g_2 = 2.016$, $g_3 = 2.003$	$Ti^{4+}–O^{\bullet -}$
O2	$g_1 = 2.025$, $g_2 = 2.015$, $g_3 = 2.003$	$Ti^{4+}–O_3^{\bullet -}$
O3	$g_1 = 2.009$, $g_2 = 2.005$, $g_3 = 2.002$	$Ti^{4+}–O_3^{\bullet -}$
R1	$g_1 = 2.035$, $g_2 = 2.008$, $g_3 = 2.002$	$C_6H_5–CH_2^{\bullet}$ (ads.)
R2	$g_1 = 2.034$, $g_2 = 2.008$, $g_3 = 2.003$	$C_6H_5–CH_2^{\bullet}$ (ads.)
T1	$g_\perp = 1.991$	Ti^{3+} in the bulk
T2	$g_\perp = 1.988$	Ti^{3+} in the bulk

Following oxygen adsorption, signals O1 and A completely disappear, while T1 remains basically unchanged (see Fig. 1c). Oxygen molecules induce dipolar broadening of the signals belonging to radicals in close vicinity, and consequently these signals vanish from the spectra. Therefore, results of Fig. 1c indicate that species associated with O1 and A features are located on the TiO_2 surface whereas Ti^{3+} centers correspond to bulk species. This observation is consistent with previous reports, which also found surface $O^{\bullet -}$ radicals upon UV illumination of TiO_2 [10,16]. Subsequently, the P25 sample was irradiated at 77 K in the presence of oxygen and evacuated for 20 min in order to remove weakly adsorbed oxygen molecules. After this treatment, signals T, and O1 are observed, along with a poorly resolved contribution at about $g = 2.010$ which modifies the shape of the spectrum in this region (Fig. 1d). This new signal is very likely related to superoxide radicals on TiO_2 formed upon capture of an electron by an oxygen molecule, whose g_2 component appears at 2.009 [8,10,16]. The low intensity of this signal contrasts results of previous studies and is probably due to hindered oxygen adsorption on a highly hydroxylated surface [17]. Adsorption of toluene vapors at 77 K only induces a slight sharpening of the spectrum, and does not produce any new features (Fig. 1e). Subsequent UV-irradiation slightly enhances the intensity of O1 signal (Fig. 1f) but it does not generate any additional signals. These results suggest that toluene does not react under these conditions with the oxygenated radicals formed on the TiO_2 surface. In particular, the increment of the intensity of the signal $O^{\bullet -}$ under irradiation in presence of toluene indicates that this organic molecule is not easily oxidised by the O1 radicals under these conditions. Neither oxygenated species nor Ti^{3+} centers are stable upon warming at RT, and consequently the only signal remaining in the spectra is A (Fig. 1g). However, UV irradiation of the cell for 30 min in the presence of toluene vapour and small amount of oxygen gives rise to a rather intense new signal, R1, with parameters $g_1 = 2.035$, $g_2 = 2.008$, and $g_3 = 2.002$ (Fig. 1h). No other significant features are observed in the spectra, apart from a slight modification of the baseline at about $g = 1.97$, which may be related to the formation of a very broad signal. On the other hand, it is worth noting that separate experiments have shown that the R1 signal is not generated if TiO_2, prior to UV-illumination, is exposed only to toluene vapors, or if the dosed mixture has a high oxygen to toluene ratio.

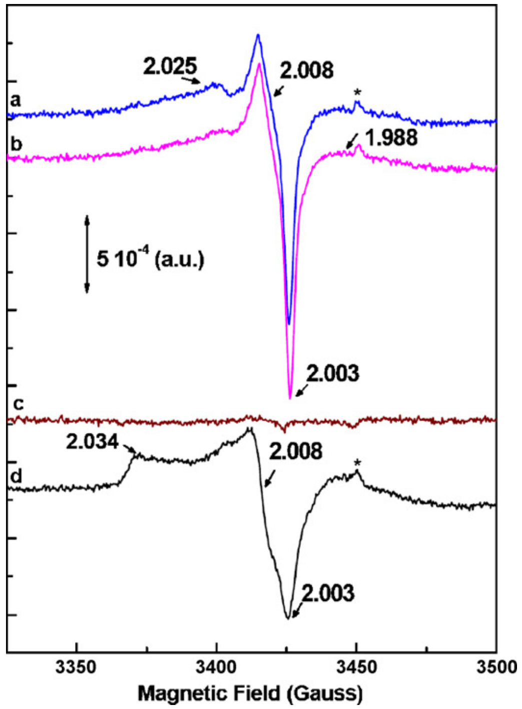

Fig. 2. EPR spectra at 77 K of (a) TiO_2 BDH outgassed at RT, exposed to oxygen at 77 K, UV-irradiated, and outgassed at 77 K for 30 min, (b) contacted with toluene at 77 K, (c) warmed to RT, and (d) UV-illuminated at 77 K. The symbol (*) marks signal due to the incomplete subtraction of background signal.

The TiO_2 BDH sample presents a relatively intense background signal which is only slightly affected by UV irradiation, and therefore it remains basically unchanged during treatment. Consequently, in order to highlight the signals of the species photogenerated, the background spectrum obtained after the vacuum treatment has been subtracted from all the spectra displayed in Fig. 2. Following UV-irradiation of the TiO_2 BDH sample in the presence of adsorbed oxygen the spectrum (Fig. 2a) shows two overlapping signal which parameters can be resolved by computer simulation: O_2 with components at $g_1 = 2.025$, $g_2 = 2.015$, and $g_3 = 2.003$, and O3 with $g_1 = 2.009$, $g_2 = 2.005$, and $g_3 = 2.002$. According to the g values, the signals O2 and O3 are ascribed to $O^{\bullet -}$ and $O_3^{\bullet -}$ adsorbed radicals, respectively Both species have been detected on UV-illuminated TiO_2 [10,11,16,18]. In addition a very broad signal, T2, at $g = 1.988$, is assigned to the $g_\perp$ component of Ti^{3+} ions in the bulk. Toluene admission in the cell does not modify the shape of the spectrum. This fact indicates that toluene does not significantly react at 77 K with the adsorbed oxygen radicals or Ti^{3+} centers. On the other hand, none of these species are thermally stable, because heating to RT, followed by cooling the cell down to 77 K results in a featureless spectrum (Fig. 2c). In contrast, subsequent irradiation of the sample, yields T2 centers, along with a rather intense signal, R2, with components at $g_1 = 2.034$, $g_2 = 2.008$ and $g_3 = 2.003$. Considering that the g tensor values of signal R2 differ only slightly from that of signal R1 detected on TiO_2 P25, it can be assumed that both correspond to basically the same radical adsorbed on sites with slightly different configuration. Although the

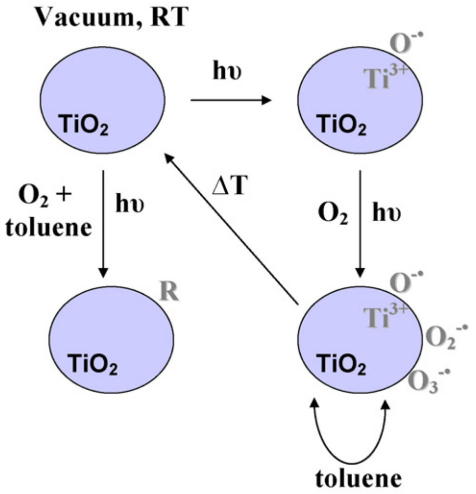

Fig. 3. Pictorial diagram showing the conditions of formation of the different radicals (in grey) detected by ESR at 77 K.

intensity of the signals obtained with the sample is higher, the mass of BDH used is 10 times higher because of the low apparent density of P25. The scheme of Fig. 3 summarizes the conditions for the formation of the different radicals species detected in this study following UV-illumination.

4. Discussion

4.1. Assignment of signals R

The signals R1 and R2 most likely correspond to the basically identical chemical species adsorbed on sites of slightly different geometry. Therefore, for sake of brevity the assignment of both features will be discussed considering only a generic R signal.

According to its origin, signal R is most likely due to an organic radical formed by partial oxidation of toluene. A reasonably candidate could be a benzyl radical, Ph-$CH_2^\bullet$, which may be produced by hole oxidation of adsorbed toluene. However, benzyl radicals adsorbed on SiO_2 present a complex hyperfine structure due ^1H coupling centered at $g = 2.00$ and consequently they are eliminated as the source of signal R [19]. Similarly, the formation of carbonyl radicals, like Ph-$CHO^\bullet$, can be also discarded on the basis of the measured g-values, which for carbonyl radicals typically range from 2.002 to 2.005 [20]. In contrast, the g-parameters of signal R are very close to those of the alkyl peroxide radicals, like those generated upon UV illumination of acetone and oxygen coadsorbed on TiO_2 [12]. In fact, the g parameters of the $ROO^\bullet$ are only slightly affected by the chemical nature of the R fragment, which in most of the cases are around $g_1 = 2.035$, $g_2 = 2.008$, and $g_3 = 2.003$ [21]. These values match almost exactly those of signal R, which therefore can be ascribed to $ROO^\bullet$ species. Hydroperoxy radicals, $HOO^\bullet$, which constitute the particular case for R = H, produce a signal with $g_1 = 2.034$, $g_2 = 2.009$, and $g_3 = 2.004$ [8]. These inorganic peroxy species can be also formed following UV-irradiation of hydrated TiO_2. However, considering that in order to produce signal R, an excess of toluene has to be present, it seems more plausible that signal R corresponds to an alkylperoxide radical. In this respect, benzylperoxy radical, Ph-$CH_2O^\bullet$, adsorbed on TiO_2 seems to be a consistent assignment, considering the high stability of the benzyl radical. To the best of our knowledge, this is the first time that such alkylperoxy species have been identified during the photocatalytic oxidation of toluene, although its formation has been previously proposed [14]. The interaction of the electron spin with a magnetic nuclei like ^1H produces the hyperfine splitting of ESR signals. The absence of any apparent hyperfine structure in signal R indicates that the splitting parameters are smaller than the width of the g components, and consequently they can only be inferred by computer simulation, as in the case of $CH_3COCH_2OO^\bullet$ radical [12]. This fact suggests a rather weak interaction of the unpaired electron with protons in the vicinity of the peroxy fragment, which also supports the assignment of signal R to Ph-$CH_2O^\bullet$ species rather than to $HO_2^\bullet$ radicals.

4.2. Initial steps of toluene photocatalytic oxidation on TiO_2

According to the ESR results, photoexcitation of TiO_2 in vacuum can be described by the equations [10,11,16]:

$$Ti^{4+} + e^- \rightarrow Ti^{3+} \tag{1}$$

$$Ti^{4+}{-}O^{2-}{-}Ti^{4+} + h^+ \rightarrow Ti^{4+}{-}O^{\bullet-}{-}Ti^{4+} \tag{2}$$

In the presence of adsorbed oxygen formation of superoxide radicals, $O_2^{\bullet-}$, by capture of photogenerated electrons occur, as it has been extensively reported [10,11,16], and the modification of the TiO_2 P25 (see Fig. 1d) spectrum suggests. In addition, TiO_2 BDH shows the formation of an additional species following the reaction [10,18]:

$$Ti^{4+}{-}O^{\bullet-}{-}Ti^{4+} + O_2 \rightarrow Ti^{4+}{-}O_3^{\bullet-}{-}Ti^{4+} \tag{3}$$

Apparently the generation of ozonide radicals, $O_3^{\bullet-}$, requires some specific surface characteristic, because these species are only detected on some TiO_2 samples.

The initial step during toluene photoxidation on the TiO_2 surface should be the reaction with hole-derived species to yield an alkyl radical [14]. In the present case, we have to consider the reaction of the organic molecule with $O^{\bullet-}$ species. However, the formation of hydroxyl radicals, $OH^\bullet$, cannot discarded on the basis of the present ESR results, because detection of these rather unstable species requires the use of spin-trapping techniques [22]. Therefore, any of the following processes could take place:

$$Ti^{4+}{-}OH^\bullet + C_6H_5{-}CH_3 \rightarrow Ti^{4+}{-}H_2O + C_6H_5{-}CH_2^\bullet \tag{4}$$

$$Ti^{4+}{-}O^{\bullet-} + C_6H_5{-}CH_3 \rightarrow Ti^{4+}{-}OH^- + C_6H_5{-}CH_2^\bullet \tag{5}$$

Formation of benzyl radical is clearly favored with regards to other possible reaction products because delocalization of the unpaired electron in the aromatic ring provides additional stability to this species. In contrast, benzene photocatalytic oxidation results in the formation of the phenyl radical, which eventually leads to the hydroxylation of the aromatic ring [23]. In any case, benzyl radicals are not detected upon UV-illumination of TiO_2 in the presence of toluene. In fact, detection of alkyl radicals like $CH_3^{\bullet}$ by ESR has been only achieved in solution in the presence of noble metal particles dispersed on $TiO_{2,}$ which act as electron drains [11]. Therefore, it seems likely that in the absence of any stabilizing factors, the equilibrium of reactions (4) and (5) is displaced to the left, and consequently the concentration of benzyl radicals is too low, even at 77 K to be detected. In contrast, when a certain amount of oxygen is present alkyl species further react to yield peroxybenzyl radicals [14] according to:

$$C_6H_5{-}CH_2^{\bullet} + O_2 \rightarrow C_6H_5{-}CH_2OO^{\bullet} \qquad (6)$$

Such species are indefinitely stable at 77 K, but if the temperature increased, production of benzaldehyde according to the following reaction is possible:

$$C_6H_5{-}CH_2OO^{\bullet} \rightarrow C_6H_5{-}CHO + OH^{\bullet} \qquad (7)$$

Benzaldehyde is frequently detected as an intermediate during the photocatalytic oxidation of toluene and accepting that reaction (7) occurs, its formation contributes to the propagation of the radical reaction. However, further oxidation of benzaldehyde can eventually lead to the formation of benzoic acid, which has been frequently associated with the deactivation of TiO_2 by blocking some of the active sites, and reducing the radical formation rate [15].

Generation of peroxy radicals in the toluene/TiO_2 system as in the acetone/TiO_2 system [12] can only take place if: (i) the organic molecule is coadsorbed with oxygen and (ii) the organic to oxygen molar ratio is at least 10. On the other hand, considering the similarities between signals R1 and R2, the production of these organic radical is not critically affected by the structural (rutile to anatase ratio) or surface characteristics (differences in the magnitude of the specific area) of TiO_2. A feasible interpretation for this behaviour is that the organic molecule must occupy some specific places that facilitate reaction with trapped holes. If oxygen is pre-adsorbed or TiO_2 is exposed to a mixture enriched in oxygen, electron transfer dominates and benzyl radicals are not detected because they are not formed or further react to diamagnetic species like benzaldehyde. Therefore, competition for adsorption sites is established between oxygen and organic molecules. This reaction scheme is supported by the fact that when peroxy radicals are detected, electrons are mainly trapped in Ti^{3+} centers and the generation of superoxide species could not be detected. However, further studies are necessary in order to confirm these mechanistic aspects.

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