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Catalytic degradation of Acid Orange 7 by H$_2$O$_2$ as promoted by either bare or V-loaded titania under UV light, in dark conditions, and after incubating the catalysts in ascorbic acid

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**Abstract**

Pure and V-loaded mesoporous titania (with 2.5 wt-% V) were prepared by template-assisted synthesis and compared to commercial titania (Degussa P25), both as such and after vanadium loading. Mesoporous TiO$_2$ occurred as pure anatase nanoparticles with higher surface area (SSA = 150 m$^2$g$^{-1}$) than P25 (SSA = 56 m$^2$g$^{-1}$). Degradation of the azo dye Acid Orange 7 by H$_2$O$_2$ was used as a test reaction: under UV light, no difference emerged between mesoporous TiO$_2$ and P25, whereas in dark conditions, higher SSA of the mesoporous sample resulted in higher conversions. Under UV illumination, surface V$^{5+}$ species inhibited photocatalytic activity, by forming inactive V$^{4+}$ species. Similarly, in dark conditions, V$^{5+}$ surface species reacted with H$_2$O$_2$, likely yielding ·O$_2$H radicals and reducing to V$^{4+}$. On the contrary, V-containing catalysts were very active after pretreatment with ascorbic acid, which reduced V$^{5+}$ species to V$^{3+}$ species, the latter promoting very lively a Fenton-like reaction.

**Keywords**

Mesoporous titania, Azo dye degradation, Hydrogen peroxide, Ascorbic acid, Fenton reaction

**Cite this article**

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**Introduction**

Titania, anatase in particular, is both a very popular photocatalyst and catalytic support, not only because of its (reasonably small) band gap, but also for the possibility of obtaining it in nanoporous and/or nanoparticle form, with increased specific surface area (SSA).\textsuperscript{8-12}

One current application of TiO$_2$ is the degradation of organic pollutants, including azo dyes, a class of organic molecules widely applied in the photographic industry (and bearing an environmental impact once released in the surroundings), which can be removed by photocatalytic degradation with TiO$_2$ usually in the presence of an oxidizing agent, like H$_2$O$_2$\textsuperscript{2}.

P25 is one of the most common commercial forms of TiO$_2$ occurring as a mixture of mainly anatase and rutile with SSA = 50 ± 15 m$^2$g$^{-1}$\textsuperscript{14}.

In the present paper, high SSA mesoporous TiO$_2$ (MT) was obtained by template-assisted synthesis, and calcined at 450°C to avoid phase transition to rutile. Anatase has, indeed, a larger adsorptive affinity than rutile for organic molecules\textsuperscript{13} and is generally regarded as the most photocatalytically active phase of TiO$_2$.\textsuperscript{1}

Since vanadium has been shown to improve the catalytic activity of TiO$_2$, extending its absorption the Vis-range, a sample of MT with a 2.5 wt-% V loading was prepared; for comparison, two samples were obtained by impregnating P25 with (i) same V content and (ii) 1/3 V content to get, in principle, the same vanadium dispersion as for V$_{2.5}$-MT.

The degradation of a model azo dye (Acid Orange 7, AO7)\textsuperscript{13} was studied either under UV illumination or not (hereafter referred to as “dark conditions”). The effects of H$_2$O$_2$ concentration in the reaction and the presence of ascorbic acid (H$_2$Asc) were also studied. H$_2$Asc, especially in biochemical processes, plays different roles as an antioxidant, a “mild” reductant of both metal ions and organic moieties, and a radical scavenger.\textsuperscript{17} It is able, inter alia, to reduce transition metal ions, including vanadium, in biological systems.\textsuperscript{18,19} Nonetheless, reports are available on the effects of an oxidant–reductant system (H$_2$O$_2$ and H$_2$Asc, for instance) in the catalytic activity of V-containing catalysts.\textsuperscript{20,21}
Experimental

Catalysts preparation

All reagents were ACS grade chemicals from Sigma-Aldrich.

The synthesis of mesoporous titania (MT) and of V-containing MT with a vanadium nominal content of 2.5 wt-% (V2.5-MT) is detailed in Ref. 23. Vanadium resulted present mainly at the surface of V2.5-MT.\textsuperscript{22} The samples were calcined at 450 °C in air to remove the template and to avoid phase transition to rutile.

The commercial titania (CT) was Degussa P25 (TiO\textsubscript{2} content ≥ 99.5%); two samples with nominal V content of either 2.5 or 0.80 wt-% (V2.5-CT and V0.80-CT) were obtained by impregnation with NH\textsubscript{4}VO\textsubscript{3} solution, followed by drying at 60 °C and calcination in air at 450 °C for 4 h.

Catalysts characterization

Powder X-ray diffraction patterns were collected on a XPert Philips PW3040 diffractometer using Cu K\textsubscript{α} radiation (2θ range = 20°–85°; step = 0.05° 2θ per step = 0.2 s) and indexed according to the Powder Data File database (PDF 2000, International Centre of Diffraction Data, Pennsylvania).

Crystallites size (D) was determined by using the Debye–Schererr formula, \( D = \frac{0.9 \lambda}{\beta \cos \theta} \), where \( \lambda \) is the wavelength of the Cu K\textsubscript{α} radiation, \( \beta \) is the full width at half maximum (in radians), 0.9 is the shape factor for spherical particles, and \( \theta \) is the angle of diffraction peaks.

The anatase content was evaluated by the full-profile Rietveld method applied to diffraction patterns using the GSAS-EXPGUI free software. XRD background was modeled by a 10-term cosine polynomial function, and pseudo-Voigt functions were adopted for peaks curve fitting.

Table 1 Textural properties as obtained by XRD diffraction, \( N_2 \) physisorption at –196 °C, and EDX chemical analysis

| Sample   | Crystallites size (nm) | \( S_{\text{BET}} \) (m\textsuperscript{2} g\textsuperscript{-1}) | Metal content (wt. %) | Surface metal density (MO\textsubscript{a} nm\textsuperscript{-2}) |
|----------|------------------------|-------------------------|----------------------|------------------------|
| MT       | 14 ± 3                 | 150                     | –                    | –                      |
| V2.5-MT  | 17 ± 5                 | 122                     | 2.5                  | 2.3                    |
| P25      | 19 ± 3 (anatase) 23 ± 4 (rutile) | 56                     | –                    | 8.7                    |
| V2.5-CT  | –                      | 39                      | 2.8                  | 2.6                    |
| V0.80-CT | –                      | 59                      | 0.77                 | –                      |

\textsuperscript{a}As calculated by applying the Debye–Schererr formula.

\textsuperscript{b}As determined by EDX analysis.

\textsuperscript{c}As obtained by applying the formula: (metal content)/(SSA × AM), where metal content is the metal weight percentage as measured by EDX, SSA is the sample specific surface area, and AM is the atomic mass of the metal.

Concerning the amount of H\textsubscript{2}O\textsubscript{2} used during experiments, the reaction leading to the complete degradation of the dye is:

\[ C_{n}H_{m}N_{x}SO_{y}Na + 42H_{2}O_{2} \rightarrow 16CO_{2} + 46H_{2}O + 2HNO_{3} + NaHSO_{4} \]  

(1)

According to reaction (1), a 0.030 M H\textsubscript{2}O\textsubscript{2} concentration roughly corresponds to the stoichiometric amount of H\textsubscript{2}O\textsubscript{2} necessary for the complete AO7 degradation, and 0.80 M H\textsubscript{2}O\textsubscript{2} to an excess of hydrogen peroxide.

A first set of catalytic tests was performed under UV light with 0.80 M H\textsubscript{2}O\textsubscript{2} by illuminating with a medium-pressure Hg lamp (Hamamatsu, LC3; light intensity of 55 mW cm\textsuperscript{-2}).

A second set of experiments was carried out in dark conditions by adding either 0.030 M or 0.80 M H\textsubscript{2}O\textsubscript{2} to the suspension containing AO7 and the solid. In a third set, 0.40 M H\textsubscript{2}Asc was added to the suspension containing AO7 and the solid, and after 20 min, 0.80 M H\textsubscript{2}O\textsubscript{2} was added in dark conditions.

In summary, a typical catalytic test involves 3.35 × 10\textsuperscript{-5} moles of AO7, either 2.45 × 10\textsuperscript{-5} or 8.17 × 10\textsuperscript{-5} moles of V, either 1.50 × 10\textsuperscript{-4} or 40.0 × 10\textsuperscript{-4} moles of H\textsubscript{2}O\textsubscript{2}. In the third set of experiments, 20.0 × 10\textsuperscript{-5} moles of H\textsubscript{2}Asc were also present. Moreover, since the mixture was not deaerated, ca. 12.3 × 10\textsuperscript{-3} moles of atmospheric O\textsubscript{2} were always present.

Aliquots of the suspension were collected at regular intervals of time, the supernatant fraction was separated by centrifugation (ALC centrifuge PK110, at 4000 rpm for 2 min) and the UV–vis spectrum was measured in the 190–800 nm range on a Cary 5000 UV–vis–NIR spectrophotometer (Varian instruments), using a quartz cell with 1-mm path length. The concentration of AO7 was evaluated by the intensity of its band at 484 nm (vide infra), after a proper calibration procedure.
Results and discussion

Survey of the main physicochemical features of the catalysts

The XRD analysis (not reported) showed that anatase is the only phase present in MT samples (99.8%, as obtained by Rietveld refinement), whereas P25 is a mixture of anatase (88.8%) and rutile (11.2%). The size of MT crystallites was around 15 nm, as calculated according to the Debye–Scherrer formula (Table 1), in agreement with previous transmission electron microscopy observation.22

Type IV 

\( \text{N}_2 \)

isotherms were measured at −196 °C on MT samples, with high SSA values due to both intra- and interparticle mesopores; a limited decrease of SSA was observed with V2.5-MT (Table 1). Fig. 1 reports DR UV–vis spectra of samples outgassed at 150 °C to remove water and other atmospheric contaminants: comparison between MT and P25 shows that the former absorbs in a broader range of wavelengths (Fig. 1a). The spectrum of MT is shifted toward higher wavelengths with respect to P25 (arrow); accordingly, the corresponding Tauc’s plots, in the version for indirect band gap (\( E_g \)) semiconductors (inset to Fig. 1a), yield \( E_g \approx 3.30 \text{ eV} \) for P25 and \( E_g \approx 3.15 \text{ eV} \) for MT. The redshift observed in MT absorption edge is likely due to slightly different optical and electrical properties of the mesoporous material with respect to bulk TiO\(_2\), as already observed with porous films of titania.23

Fig. 1b compares the UV–vis spectra of V-containing catalysts, characterized by a pale yellow color: with respect to parent MT, V2.5-MT shows a small redshift of the absorption band and an increased absorption above 375 nm. Both isolated VO\(_x\) and oligomeric V\(_{x}\)O\(_y\) species (\( y = 2x + 1 \) in dehydrated powders), respectively, absorbing at 270 and 325 nm,24,25 are likely present at the surface, though their occurrence is masked by TiO\(_2\) absorption. V2.5-CT has similar UV–vis spectrum, whereas absorption related to VO\(_x\) species is less intense with V0.80-CT, in agreement with the lower metal content.

Preliminary considerations about catalytic tests

Scheme 1 reports the possible structures of AO7 in water: the hydrazone form (B), stable in the solid phase, undergoes, in water, azo-hydrazone tautomerism via intramolecular proton transfer, so that both hydrazone (B) and azo-form (A) are simultaneously present in solution.

The UV–Visible spectrum of 0.67 mM AO7 in water is reported as the bold curve in Fig. 2: the two peaks at 310 and 230 nm and the shoulder at 256 nm are due to aromatic ring absorptions. The peak at 484 nm is due to the n–\( \pi^* \) transition involving the lone pair on the \( \text{N} \) atoms and the conjugated system extending over the two aromatic moieties and encompassing the \( N–N \) group of the hydrazone form.26 The shoulder at 403 nm has a similar nature, involving the \( N–N \) group of the azo-form.26

The (non-catalytic) reaction between AO7 and H\(_2\)O\(_2\) (either 0.030 M or 0.80 M) was preliminarily studied. The UV–vis spectra taken with 0.80 M H\(_2\)O\(_2\) are reported in Fig. 2: the region below 300 nm is dominated by H\(_2\)O\(_2\) absorption; small changes are observed in the AO7 bands, for which a limited decrease in intensity is observed after 24 h, as H\(_2\)O\(_2\) is, per se, able to attack aromatic rings.27 This shows that without catalyst, a limited conversion of AO7 is obtained, even in the presence of excess H\(_2\)O\(_2\).

Catalytic tests under illumination

Fig. 3 compares results obtained after 20-min UV illumination without H\(_2\)O\(_2\); in such conditions, the oxidizing agent is dissolved oxygen. UV irradiation, in turn, generates electron (\( e^- \))/hole (\( h^+ \)) pairs in TiO\(_2\). Dissolved O\(_2\) most probably acts as...
an acceptor of e− (equation (2)) and the powerful oxidant h+ reacts with OH− ions, generating radical HO· species (equation (3)) taking part in the AO7 degradation:

\[ \text{O}_2 + e^- \rightarrow \text{O}_2^- \quad \text{(2)} \]

\[ \text{OH}^- + h^+ \rightarrow \text{HO} \quad \text{(3)} \]

The MT and P25 had the same photocatalytic activity (Fig. 3a), whereas V2.5-CT and V2.5-MT (Fig. 3b) were practically inactive. The same behavior of the bare TiO₂ samples, notwithstanding the different SSA, may be surprising. It has to be recalled, however, that P25, an optimized commercial sample, contains a substantial fraction of rutile, which is recognized to be able to prevent the fast electron–hole recombination occurring in anatase, due to a positive synergic effect between anatase and rutile nanoparticles in P25.¹⁴,²⁸

The inactivity of V-containing TiO₂ has another explanation: surface V⁵⁺ centers may trap electrons, giving rise to reduced (and probably inactive) V⁴⁺ species. Inhibition of TiO₂ reactivity by surface V species is probably related to the fact that the latter act as recombination centers for electron–hole pairs, eventually suppressing the intrinsic photocatalytic activity of the support. This is in agreement with previous literature results, showing that vanadium has a detrimental effect on the photocatalytic activity of V-doped TiO₂ under UV light, though extending absorption in the Vis range.¹⁶

Results obtained under UV light with 0.030 M H₂O₂ are reported in Fig. 4: as expected, addition of H₂O₂ to the reaction mixture had a positive effect on the photocatalytic activity of all the samples. With pure TiO₂ (Fig. 4a), H₂O₂ most probably acts as an acceptor of photogenerated electrons (e−), according to reaction (4):

\[ \text{H}_2\text{O}_2 + e^- \rightarrow \text{OH}^- + \text{HO} \quad \text{(4)} \]

forming hydroxyl radicals for the degradation of AO7. Again, MT and P25 show the same activity as before, and V has almost no effect on photocatalytic activity (Fig. 4b), which seems only due to TiO₂⁺.

**Catalytic behavior in dark conditions**

Successive tests were run without UV irradiation to exploit the mere surface properties of the catalysts.

Fig. 5a reports, as an example, spectra obtained after contacting AO7 solution with MT sample and 0.030 M H₂O₂ in dark conditions; Fig. 5b reports results obtained in dark conditions with the same catalyst and 0.80 M H₂O₂. In both cases, bands of AO7 decreased in intensity: no new band, related to any decomposition product, however, appeared. As shown in Fig. 2, the spectral region below 300 nm is dominated by H₂O₂ absorption at higher concentration of the reactant: this feature was observed with all catalysts, so that the presence, if any, of reaction products absorbing in this region was not detectable. On the other hand, the intensity of the absorption below 340 nm does not decrease, so showing that the 0.80 M solution provides excess H₂O₂ in agreement with previous stoichiometric considerations.

Fig. 6 reports conversions obtained with all the studied catalysts in the same conditions (i.e. dark conditions and 0.80 M H₂O₂): MT at any reaction time exhibits conversion values about double than P25, in agreement with the higher SSA. The same explanation holds for the higher activity of V2.5-MT, with respect to both V2.5-CT and V0.80-CT samples, which showed similar curves, independently of the V content, indicating a worse vanadium dispersion attained with P25.

Table 2 reports values of final conversion (Fig. 6) and initial rate obtained in dark conditions with either 0.030 M or 0.80 M H₂O₂: as expected, final conversion always increases with H₂O₂ concentration and in the presence of a catalyst. Conversely, higher initial rates are observed at lower H₂O₂ concentration. Successive tests were run without UV irradiation to exploit the mere surface properties of the catalysts. With pure TiO₂ (Fig. 4), H₂O₂ most probably acts as an acceptor of photogenerated electrons (e−), according to reaction (4):

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\[ \text{H}_2\text{O}_2 + \text{HO}^- \rightarrow \text{H}_2\text{O} + \cdot \text{O}_2\text{H} \quad \text{(5)} \]

With respect to P25, conversion reached with MT is higher, in agreement with the higher SSA of the latter catalyst; concerning initial rate, the positive effect of MT SSA may be appreciated at 0.80 M H₂O₂ concentration (Table 2).

Reactivity of Ti with H₂O₂ is well documented in the literature as it concerns Ti-Silicalite, and involves formation of...
titania\textsuperscript{31,32} supporting the idea of the formation of reactive Ti–OOH groups, which are responsible for the catalytic activity of MT. The “quenching effect” of H\textsubscript{2}O\textsubscript{2} observed at higher concentration (Table 2) is in agreement with the hypothesis of a radical mechanism, in which reactive OH\textsuperscript{•} species are, in this case, due to decomposition of Ti–OOH.

Table 2 shows that with 0.030 M H\textsubscript{2}O\textsubscript{2}, initial rates are higher in the presence of V\textsubscript{2.5}-MT and V\textsubscript{2.5}-CT catalysts, whereas with 0.80 M H\textsubscript{2}O\textsubscript{2} V-containing samples are very active at the peroxo bridges with expansion of the coordination sphere of Ti.\textsuperscript{30} Concerning TiO\textsubscript{2}, in the presence of H\textsubscript{2}O\textsubscript{2}, surface Ti–OH groups are partially converted into Ti–OOH species, more reactive than H\textsubscript{2}O\textsubscript{2} in partial oxidation reactions.\textsuperscript{31}

Fig. 7 reports XPS spectra of MT before and after reaction with 0.80 M H\textsubscript{2}O\textsubscript{2}, for Ti 2p (section a) and O 1s range (section b). Before reaction, with MT, two peaks are seen at 464.02 and 458.28 eV, respectively, assigned to the 2p\textsubscript{1/2} and 2p\textsubscript{3/2} lines of Ti\textsuperscript{4+},\textsuperscript{32} the spectrum of P25 being very similar. After reaction, MT XPS spectrum shifts to higher BE values: the same behavior, observed for anatase treated with H\textsubscript{2}O\textsubscript{2},\textsuperscript{32} was ascribed to the formation of surface Ti–OOH groups, as the peroxy group has an electron-withdrawing effect and causes a shift to higher BE values.\textsuperscript{32}

The O 1s region of MT and P25 XPS spectra is similar before reaction: that of MT shifts to higher BE values after reaction. This could be ascribed to a more extensive formation of Ti–OOH species in MT, due to the higher SSA. Curve fits of the O 1s range are reported for MT in Fig. 7c and d: before reaction, a satisfactory curve fit was obtained with two peaks at 529.53 and 530.90 eV, due to O\textsuperscript{2−} related to Ti\textsuperscript{4+} and to OH\textsuperscript{−} species, respectively. Conversely, after reaction, a satisfactory group curve fit was obtained with three peaks, the additional peak at 532.33 eV being ascribed to Ti–OOH species.\textsuperscript{32} Although based on delicate curve fitting procedures, such result is in agreement with previous literature reports on H\textsubscript{2}O\textsubscript{2}-treated titania\textsuperscript{31,32} supporting the idea of the formation of reactive Ti–OOH groups, which are responsible for the catalytic activity of MT.

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and a sudden initial increase and so the activity of doped surfaces should thus be not only to metal sites, but also to such patches.

In agreement with the literature, we propose that reduction of V$^{5+}$ to V$^{4+}$ species occurs according to the reactions (6) and (7):

\begin{align*}
\text{(6)} \quad & \text{V}^{5+} + e^- \rightarrow \text{V}^{4+} \\
\text{(7)} \quad & \text{V}^{4+} + \text{H}_2 \rightarrow \text{V}^{3+} + \text{H}_2\text{O}
\end{align*}

At the beginning of the reaction, then conversion reaches a plateau (Fig. 6), indicating that they are subjected to deactivation. The surface density of heteroatoms (Table 1) is low; therefore, catalytically active patches of TiO$_2$ still occur at the surface. The curve conversion vs. time of V-containing samples is describable as the superposition of the corresponding undoped TiO$_2$ and a sudden initial increase and so the activity of doped surfaces should thus be not only to metal sites, but also to such patches.

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\end{align*}
V⁴⁺ is formed together with a hydroperoxyl radical HO₂⋅ that can react with excess H₂O₂ forming more reactive HO⋅ (equation (8)). Such process is not catalytic, but stoichiometric, and indeed vanadium effect is only observed at the beginning of the reaction, the final conversion being almost the same as with bare TiO₂. If the MT conversion curve is subtracted from that of V₂.5-MT, indeed, only 10% AO7 results to be converted by surface vanadium species, indicating that a limited fraction of surface V sites is reactive.

Formation of surface V⁴⁺ species is confirmed by XPS measurement run V₂.5-MT: before reaction, two peaks are seen at 525 and 510 eV, whereas after reaction, only one peak at 520 eV is observed, indicating the formation of V⁴⁺ species.

The reaction mechanism can be summarized as follows:

\[ \equiv V + O + H₂O₂ \rightarrow \equiv V(OOH)OH \quad (6) \]

\[ \equiv V - (OOH)OH \rightarrow \equiv V(\cdot OH) + HO₂ \quad (7) \]

\[ \text{HO₂} \cdot + \text{H₂O₂} \rightarrow \text{HO} \cdot + \text{H₂O} + \text{O}_2 \quad (8) \]

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H₂Asc is mostly adsorbed at the surface of titania through the reaction:

$$\text{Ti-OH} + \text{H}_2\text{Asc} \rightarrow \text{Ti-OAH} + \text{H}_2\text{O}$$  \hspace{1cm} (9)$$

decreasing the amount of surface Ti–OH, so that less sites are available for the formation of Ti–OOH species by interaction with H₂O₂.

With V2.5-MT, 100% conversion is reached in few minutes (Fig. 11b); the same effect was observed with both V2.5-CT and V0.80-CT.

V³⁺ surface species are likely reduced by H₂Asc to V⁴⁺ species, which may undergo Fenton-like reaction switching to V⁵⁺:

$$\text{V}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{V}^{4+} + \text{OH}^- + \cdot\text{HO}$$  \hspace{1cm} (10)$$

$$\text{V}^{4+} + \text{H}_2\text{O}_2 \rightarrow \text{V}^{3+} + \cdot\text{H} + \text{HO}_2^-$$  \hspace{1cm} (11)

$$\text{HO}^- + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^- + \text{H}_2\text{O}$$  \hspace{1cm} (12)

$$\text{HO}_2^- + \text{H}_2\text{O}_2 \rightarrow \text{HO}^- + \text{H}_2\text{O} + \text{O}_2$$ \hspace{1cm} (13)

AO7 + HO⁻ → degradation products  \hspace{1cm} (14)

In this case, the presence of an excess of H₂Asc ensured reduction of all surface species and allowed several redox cycles, in which very reactive V³⁺ species were regenerated, avoiding catalyst deactivation due to formation of V⁴⁺.

**Effect of ascorbic acid on catalytic activity in dark conditions**

H₂Asc, a well-known reducing agent, was used to reduce vanadium to V³⁺ species, which are active in the Fenton-like reaction (**vide infra**). Blank experiments without any catalyst were firstly run by contacting 0.67 mM AO7 solution with either 0.40 M H₂Asc or 0.80 M H₂O₂ and with both chemicals (0.40 M H₂Asc and 0.80 M H₂O₂). Fig. 9 compares the related UV–vis spectra: curve 2 is obtained with 0.40 M H₂Asc after 120-min contact, showing that some reaction occurs between AO7 and H₂Asc, whereas the strong absorption below 320 nm is due to H₂Asc itself. AO7 conversion after 90 min with 0.80 M H₂O₂ is ca. 5.0% (curve 3), the intense absorption below 280 nm being due to H₂O₂. When both H₂A and H₂O₂ are present (curve 4), the band of H₂Asc decreases, due to reaction with H₂O₂.

Fig. 10 reports UV–vis spectra obtained with MT a and V2.5-MT b in the presence of 0.40 M H₂Asc (curves 2) and 20 min after addition of 0.80 M in the presence of 0.40 M H₂Asc, whereas Fig. 11 compares catalytic activities in dark conditions with and without H₂Asc. H₂Asc depresses the activity of MT; the conversion remaining constant to a value well below that obtained without H₂Asc (Fig. 11a). In agreement with the literature,[^46^] H₂Asc is mostly adsorbed at the surface of titania through the reaction:

$$\text{Ti-OH} + \text{H}_2\text{A} \rightarrow \text{Ti-OAH} + \text{H}_2\text{O}$$ \hspace{1cm} (9)$$

decreasing the amount of surface Ti–OH, so that less sites are available for the formation of Ti–OOH species by interaction with H₂O₂.

With V2.5-MT, 100% conversion is reached in few minutes (Fig. 11b); the same effect was observed with both V2.5-CT and V0.80-CT.

V³⁺ surface species are likely reduced by H₂A to V⁴⁺ species, which may undergo Fenton-like reaction switching to V⁵⁺:

$$\text{V}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{V}^{4+} + \text{OH}^- + \cdot\text{HO}$$  \hspace{1cm} (10)$$

$$\text{V}^{4+} + \text{H}_2\text{O}_2 \rightarrow \text{V}^{3+} + \cdot\text{H} + \text{HO}_2^-$$  \hspace{1cm} (11)

$$\text{HO}^- + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^- + \text{H}_2\text{O}$$  \hspace{1cm} (12)

$$\text{HO}_2^- + \text{H}_2\text{O}_2 \rightarrow \text{HO}^- + \text{H}_2\text{O} + \text{O}_2$$ \hspace{1cm} (13)

AO7 + HO⁻ → degradation products  \hspace{1cm} (14)

In this case, the presence of an excess of H₂Asc ensured reduction of all surface species and allowed several redox cycles, in which very reactive V³⁺ species were regenerated, avoiding catalyst deactivation due to formation of V⁴⁺.

**Conclusions**

In dark conditions, MT is more active than P25 in the degradation of AO7, likely due to its larger SSA, which favors the formation of reactive Ti–OOH species in the presence of H₂O₂; under UV illumination, the two types of TiO₂ showed comparable activity, due to a balance between higher SSA of MT and mixed crystalline composition of P25.

Absorption of UV light gives rise to the formation of inactive V⁴⁺ species, and therefore, surface doping with V may be detrimental to photocatalytic activity. In dark conditions, V³⁺ species are reduced by H₂O₂, to the same inactive V⁴⁺ ions, but after contact with H₂Asc, reduction to V³⁺ species occurs, the latter species being, instead, very active in a Fenton-like mechanism.

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[^46^]: Ti-OH + H₂Asc → Ti-OAH + H₂O

[^41^]: V³⁺ + H₂O₂ → V⁴⁺ + OH⁻ + HO⁻

[^42^]: V⁴⁺ + H₂O₂ → V³⁺ + OH⁻ + HO₂⁻
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