Impact of H$_2$O$_2$ on the Lactic and Formic Acid Degradation in Presence of TiO$_2$ Rutile and Anatase Phases under UV and Visible Light

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Abstract: The degradation rates of formic acid and lactic acid in the presence and absence of H$_2$O$_2$ were studied, utilizing several TiO$_2$ catalysts: PC105 (100% anatase), MPT 625 (100% rutile), and P25 (80% anatase/20% rutile), and the results were discussed with regards to the current literature. The impact of hydrogen peroxide on the photocatalytic efficiency of eleven TiO$_2$ samples was then determined, using commercial anatase structures (PC105, PC500, UV100), commercial mixed anatase/rutile (P25 and P90), and six rutile (two commercial samples: MPT 625 and C-R160, and four home-made rutile samples were synthesized by TiCl$_4$ hydrolysis). The effect of catalyst surface area and TiO$_2$ phase on the degradation rate of lactic acid (LA) and the decomposition of H$_2$O$_2$ was studied and discussed in regard to the active species generated. The intermediate products formed in the absence and presence of H$_2$O$_2$ were also an important factor in the comparison. Finally, the efficiency of the degradation of LA and formic acid (FA) in the presence of rutile and H$_2$O$_2$ was determined under visible light, and their reactivity was compared. The intermediate products formed in the degradation of LA were identified and quantified and compared to those obtained under UV (Ultra-Violet).

Keywords: photocatalysis; UV; visible light; TiO$_2$; rutile; anatase; H$_2$O$_2$

1. Introduction

Several publications [1–14] have mentioned the impact that H$_2$O$_2$ addition has on the degradation of different organic compounds in the presence of TiO$_2$. Most studies performed using P25 TiO$_2$ found that H$_2$O$_2$ has a favorable impact. It was explained by the elevated hydroxyl radical production, either due to hydrogen peroxide’s reaction with conduction band electrons, or to indirect formation via O$_2^{-}$, which is generated by the reduction of water and is able to avoid electron–hole recombination (Equations (1) and (2)).

\[
\begin{align*}
H_2O_2 + e^- & \rightarrow \text{OH}^+ + \text{OH}^- \quad (1) \\
H_2O_2 + O_2^{-} & \rightarrow \text{OH}^+ + \text{OH}^- + O_2 \quad (2)
\end{align*}
\]
However, some researchers have also shown an unfavorable effect of H$_2$O$_2$ on TiO$_2$ [2,3] which is explained by the competition between photogenerated holes, since H$_2$O$_2$ competes with the reaction of water (Equation (3)), which limits the formation of OH radicals (Equations (3) and (4)):

\[
\text{H}_2\text{O}_2 + h^+ \rightarrow \text{H}^+ + \text{HO}_2^- \tag{3}
\]

\[
\text{H}_2\text{O} + h^+ \rightarrow \text{H}^+ + \text{OH}^- \tag{4}
\]

To our knowledge, the impact of anatase and rutile phase on the UV degradation of organic molecules in the presence of H$_2$O$_2$ has not been well studied, and the interpretation of the results is still under debate [1,15]. H$_2$O$_2$ seems to always have a higher impact in the presence of rutile TiO$_2$ under UV irradiation. While differences in the nature of peroxo-complex formation on the surface of anatase and rutile phases was suggested by Ohno et al. [1], Tang et al. [15] reported that the difference could be attributed to a heterogeneous reaction on the particle surface of the photocatalyst for anatase TiO$_2$, and a reaction in solution for rutile TiO$_2$.

Contrary to the latter hypothesis, it is well known that in the presence of H$_2$O$_2$ a complex is formed on the surface of TiO$_2$, allowing for H$_2$O$_2$ decomposition. Moreover, several publications report the decomposition of this peroxo-complex on rutile and anatase phase in the absence of pollutants and show that the decomposition of H$_2$O$_2$ is favored on rutile phase. These results are in agreement with the work of Hirakawa et al. [16] and Zhang et al. [17]. Both publications provide evidence of an increase in OH$^-$ radical formation by the addition of hydrogen peroxide on rutile and rutile-containing TiO$_2$, and a decrease in O$_2$$^{-\circ}$ formation. For anatase TiO$_2$, a decrease in OH$^-$ radical formation and an increased formation of O$_2$$^{-\circ}$ were observed. However, to our knowledge, no connections have been made in previous works on the impact that pollutants have on these results.

Several other works were also published on the possibility of using visible light to degrade pollutants in the presence of TiO$_2$ and H$_2$O$_2$, and have mentioned the activation of the peroxo-complex formed on the surface of TiO$_2$ [15,18–21]. However, no comparison was made between the impact of H$_2$O$_2$ on the efficiency of TiO$_2$ under UV and visible light.

Many other issues remain subject to debate: is the favorable or unfavorable impact of H$_2$O$_2$ dependent on the surface area of the catalyst? Is there a correlation between the disappearance rate of organic compounds and the disappearance rate of H$_2$O$_2$? What is the impact of H$_2$O$_2$ on the formation of intermediate products? What is the efficiency of H$_2$O$_2$/rutile under visible light in comparison to UV? Is the mechanism similar under UV and visible activation?

The objective of our work is to try to answer to some of these questions using two pollutants: formic acid and lactic acid. We also plan to utilize several rutile, anatase and mixed phase photocatalysts with varying surface areas under UV irradiation. Finally, we plan to draw a comparison between the H$_2$O$_2$/rutile efficiency under UV and visible light using formic acid and lactic acid.

2. Results and Discussion

2.1. Comparison of the Impact of H$_2$O$_2$ on Formic and Lactic Acid Photocatalytic Degradation in Presence of P25, PC105 and C-R100

Before studying the impact of H$_2$O$_2$ on formic acid and lactic acid degradation, a control experiment was carried out with H$_2$O$_2$ in the dark. No oxidation of formic acid and lactic acid was observed within a 2 h period of darkness at room temperature, indicating that the possible degradation of hydrogen peroxide in the absence of light can be ruled out for all experiments. Similarly, control experiments using UV irradiation in the absence of a photocatalyst (while maintaining constant pollutant and H$_2$O$_2$ concentrations) confirm the lack of photolysis.

The impact of H$_2$O$_2$ on lactic acid and formic acid was then determined in the presence of three commercial TiO$_2$ samples: PC105, C-R100 and P25—a commonly used reference in photocatalysis.
The disappearance rate of these two organic compounds was represented as a function of time in the presence and absence of H$_2$O$_2$ (Figure 1).

Regardless of which organic compound was used, the same behavior was observed: a significant improvement of the degradation rate in the presence of rutile phase TiO$_2$ (Figure 1a,c,d,f), and no impact or a slightly negative impact in the presence of pure anatase phase.

Few works have studied the impact of the anatase and rutile phase on the degradation of organic molecules in the presence of H$_2$O$_2$, and the interpretation of their results is still subject to debate [1,15]. In all cases, the authors found that H$_2$O$_2$ had a greater impact in the presence of rutile TiO$_2$ and under UV irradiation, which agrees with our results. While Ohno et al. [1] suggested that the difference is due to the nature of the H$_2$O$_2$ complex formed, Tang et al. [15] suggested that photodegradation catalyzed...
by rutile TiO$_2$ occurs mainly in the solution, but takes place on the surface of the photocatalyst when anatase TiO$_2$ is present.

Further explanations have been published using experiments performed in the absence of pollutant $^{[16,17,22]}$, which show a difference in the nature of Reactive Oxygen Species (ROS) generation on the two TiO$_2$ phases in the presence of H$_2$O$_2$. The authors found that when H$_2$O$_2$ is utilized, hydroxyl radicals (OH$^-$) are primarily generated on rutile TiO$_2$, while in the presence of anatase TiO$_2$, hydroperoxide radical (HO$_2^+$) (a much fewer active species) formation predominates $^{[16,17]}$. These differences are explained by the formation of alternate H$_2$O$_2$ complexes on TiO$_2$: Ti–$\eta^2$-peroxide on the surface of rutile, and Ti–$\mu$-peroxide on the surface anatase $^{[17]}$. Although Density Functional Theory (DFT) analyses indicate that for both phases the more favorable structure of the Ti-peroxo-complex is Ti–O–O–H $^{[23,24]}$.

The differences in the reduction and oxidation properties of these two phases were suggested by our previous results $^{[22]}$ and evaluated by the determination of conduction band energies $^{[25]}$. It was found that the Conduction Band (CB) edge of rutile TiO$_2$ is localized at a lower potential than the CB of anatase, inducing a stronger reducing potential for rutile TiO$_2$. On the surface of rutile TiO$_2$, a direct reduction of H$_2$O$_2$ or indirect reaction between O$_2$$^{-\cdot}$ and H$_2$O$_2$ (Equations (1) and (2)) would likely occur. While on anatase TiO$_2$, due to its stronger oxidizing potential, H$_2$O$_2$ is primarily oxidized into HO$_2^+$ (Equation (3)) in competition with water (Equation (4)).

According to these various studies, the greater impact of H$_2$O$_2$ on rutile phase TiO$_2$ can be explained by a higher production of OH$^-$ due to differences in the oxydo-reduction properties of rutile and anatase.

2.2. Impact of H$_2$O$_2$ on the Photocatalytic Degradation of Lactic in Presence of Different TiO$_2$ Rutile, Anatase and Mixture of These Both Phases

The impact of hydrogen peroxide on lactic acid (LA) degradation was determined in the presence of two commercial rutile, three commercial anatase, and two mixed phase TiO$_2$ samples. Experiments were also conducted using four home-made rutile samples. The LA degradation rates obtained in the presence and absence of H$_2$O$_2$ are reported in Figure 2a.

As formerly observed and discussed in the previous paragraph, a substantially positive impact on rutile TiO$_2$ (C-R160 is an exception) was observed, while no impact or a slightly negative impact was observed for the pure anatase phase, shown in Figure 2b by representing the ratio of the LA degradation rate with and without H$_2$O$_2$.

In addition to differences between the rutile and anatase phases, some differences are also observed within the same phase. H$_2$O$_2$ had a significantly positive impact on our two home-made TiO$_2$ rutile samples, which were both calcined after 2 and 48 h of hydrolysis. Improvement factors of 10 and 18 were found, respectively. Moreover, the lactic acid degradation rates on these two catalysts in the presence of H$_2$O$_2$ are about 1.4 times higher than that of TiO$_2$ P25, an international reference in the photocatalytic field.

The lack of a positive impact on LA degradation in the presence of C-R160 and its low efficiency are attributed to the presence of surface impurities observed by the release of organic acid in water, and by the presence of about 5% Si. On the one hand, the presence of SiO$_2$ on TiO$_2$ surface modifies the adsorption properties of LA due to the ZPC (zero point charge) of silica which is about 2 and favors the recombination of (e$^-$, h$^+$) pairs, on the other hand, the organic impurities present in C-R160 are degraded in competition with LA degradation.
The authors found that when H₂O₂ is utilized, hydroxyl radicals (OH°) are primarily generated on rutile TiO₂, while in the presence of anatase TiO₂, hydroperoxide radical (HO₂°) (a much fewer active species) formation predominates [16,17]. These differences are explained by the formation of alternate H₂O₂ complexes on TiO₂: Ti–η₂-peroxide on the surface of rutile, and Ti–μ-peroxide on the surface anatase [17]. Although Density Functional Theory (DFT) analyses indicate that for both phases the more favorable structure of the Ti–peroxo-complex is Ti–O–O–H [23,24].

The differences in the reduction and oxidation properties of these two phases were suggested by our previous results [22] and evaluated by the determination of conduction band energies [25]. It was found that the Conduction Band (CB) edge of rutile TiO₂ is localized at a lower potential than the CB of anatase, inducing a stronger reducing potential for rutile TiO₂. On the surface of rutile TiO₂, a direct reduction of H₂O₂ or indirect reaction between O₂°− and H₂O₂ (Equations (1) and (2)) would likely occur. While on anatase TiO₂, due to its stronger oxidizing potential, H₂O₂ is primarily oxidized into HO₂°− (Equation (3)) in competition with water (Equation (4)).

According to these various studies, the greater impact of H₂O₂ on rutile phase TiO₂ can be explained by a higher production of OH° due to differences in the oxydo-reduction properties of rutile and anatase.

2.2. Impact of H₂O₂ on the Photocatalytic Degradation of Lactic in Presence of Different TiO₂ Rutile, TiO₂ Anatase and Mixture of These Both Phases

The impact of hydrogen peroxide on lactic acid (LA) degradation was determined in the presence of two commercial rutile, three commercial anatase, and two mixed phase TiO₂ samples. Experiments were also conducted using four home-made rutile samples. The LA degradation rate of lactic acid (LA (+H₂O₂))/r(LA (-H₂O₂)) (Figure 2).

The slightly improved efficiency of MPT-625 (C-R100) towards lactic acid degradation in the presence of H₂O₂ could be partly attributed to the photo-Fenton reaction caused by the presence of iron in the structure, which was observed by Inductively Coupled Plasma (ICP) and X-ray photoelectron spectrometry (XPS).

Considering our home-made rutile TiO₂ samples, the most efficient catalysts are those which have been calcined at 300 °C. A likely cause is the improvement in crystallinity which favors the formation of OH° radicals. It can also be attributed to a decrease in pore volume. After calcination, the volume of the pores are 2.2 and 1.7 10⁻² cm³ g⁻¹ for HM-R2c and HMr-R48c, respectively, while prior to calcination, the pore volumes were 0.7 and 0.9 10⁻² cm³ g⁻¹ [18].

Moreover, it is apparent that the larger the surface area, the less lactic acid is degraded in the presence of H₂O₂ (Figure 3). Similar behavior was also observed for the pure anatase phase (Figure 3). While the impact is significant on the rutile phase, in the presence of pure anatase or anatase mixed with 20% rutile TiO₂, an increase in the surface area has much less of an impact.
with the impact that H$_2$O$_2$ could be partly attributed to the photo-Fenton reaction caused by the presence of iron in the structure, which was observed by Inductively Coupled Plasma (ICP) and X-ray photoelectron spectrometry (XPS).

Regardless of which TiO$_2$ phase is used, the degradation of LA in the presence of H$_2$O$_2$ is directly linked to the adsorption properties of LA due to the ZPC (zero point charge) of silica which is about 2 and 10 H$_2$O$_2$ complexes on the surface of TiO$_2$ leading to a greater formation of reactive oxygen species (ROS). These results agree with the impact that H$_2$O$_2$ degradation has on LA degradation (Figure 5).

As formerly observed and discussed in the previous paragraph, a substantially positive impact was observed for the pure anatase phase, shown in Figure 2b by representing the ratio of the LA degradation rate with and without H$_2$O$_2$.

Moreover, the lactic acid degradation rates on these two catalysts in the presence of H$_2$O$_2$ are about 1.4 times higher than that of TiO$_2$ P25, an international reference in pure rutile, anatase, and mixed phase TiO$_2$. The dashed horizontal line corresponds to a ratio of 1 (LA degradation rate equivalent in the presence or absence of H$_2$O$_2$).

Figure 4. LA degradation rate in the presence of rutile TiO$_2$ (filled squares), anatase TiO$_2$ (diamonds), and mixed anatase/rutile TiO$_2$ (cross) as a function of LA adsorption.

Considering our home-made rutile TiO$_2$ samples, the most efficient catalysts are those which are attributed to the presence of surface impurities observed by the release of organic acid in water, leading to a greater formation of reactive oxygen species (ROS). These results agree with the impact that H$_2$O$_2$ degradation has on LA degradation (Figure 5).

Figure 3. Impact of the surface area on LA degradation in the presence of rutile TiO$_2$ (filled square), anatase TiO$_2$ (diamond) and mixed anatase rutile phase (cross).

Considering lactic acid adsorption, the pollutant degradation rate in the presence of H$_2$O$_2$ tends to decrease with increasing adsorption; however, this decrease seems to depend on the TiO$_2$ phase type (Figure 4). This behavior can be explained by an enhancement in the formation of H$_2$O$_2$ complexes on the surface of TiO$_2$ leading to a greater formation of reactive oxygen species (ROS). These results agree with the impact that H$_2$O$_2$ degradation has on LA degradation (Figure 5).
Figure 3. Impact of the surface area on LA degradation in the presence of rutile TiO$_2$ (filled square), anatase TiO$_2$ (diamond) and mixed anatase rutile phase (cross).

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Figure 4. LA degradation rate in the presence of rutile TiO$_2$ (filled squares), anatase TiO$_2$ (diamonds), and mixed anatase/rutile TiO$_2$ (cross) as a function of LA adsorption.

Regardless of which TiO$_2$ phase is used, the degradation of LA in the presence of H$_2$O$_2$ is directly correlated to the decomposition of H$_2$O$_2$ as observed in Figure 5. This clearly indicates that the degradation of lactic acid is due to the activation of the complex formed between TiO$_2$ and H$_2$O$_2$.

While our results clearly show that LA degradation is correlated to the decomposition of an H$_2$O$_2$ complex formed on the surface of TiO$_2$, the negative impact of the surface area on the LA degradation rate is difficult to understand. Indeed, in the absence of H$_2$O$_2$, increasing the surface area of TiO$_2$ improves pollutant degradation [22,26]. In combination with our results showing the decomposition of H$_2$O$_2$ increasing as a function of the surface area, LA degradation should also increase with surface area. However, this is not the case. Moreover, we observe that depending on the nature of the TiO$_2$ phase, the impact of the surface area differs. A more negative impact was found for rutile TiO$_2$, whereas the surface area has much less of an impact on anatase TiO$_2$.

This behavior could be explained by an increase in the deactivation of reactive oxygen species on the surface of TiO$_2$ with increasing surface area. The varying degree of deactivation on anatase and rutile phases is potentially due to the different active species generated due to the more important amount of H$_2$O$_2$ adsorbed on important surface area. Active species initially formed could react with the more important amount of H$_2$O$_2$ adsorbed on more important surface area.

On rutile TiO$_2$, OH$^\circ$ generated by the decomposition of peroxo-complexes can react with H$_2$O$_2$ forming HO$_2^\circ$, a less active species in comparison to OH$^\circ$ (Equation (5)):

$$\text{OH}^\circ + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^\circ + \text{H}_2\text{O}$$  \hspace{1cm} (5)

While HO$_2^\circ$, which is generated in the anatase phase, can react with H$_2$O$_2$ to form OH$^\circ$, this limits the negative impact of the surface area (Equation (6)):

$$\text{HO}_2^\circ + \text{H}_2\text{O}_2 \rightarrow \text{OH}^\circ + \text{H}_2\text{O} + \text{O}_2$$  \hspace{1cm} (6)

However, it is just a hypothesis which should be verified by determining the active species generated using a high surface area of TiO$_2$ compared to the small surface area of TiO$_2$. 

Figure 5. Lactic acid degradation rate as a function of H$_2$O$_2$ degradation rate for various TiO$_2$ samples.
2.3. Impact of H$_2$O$_2$ on the Chemical Pathways of Lactic Acid Photocatalytic Degradation

Two initial chemical pathways can occur during the degradation of lactic acid: either decarboxylation or dehydrogenation, giving ethanol and pyruvic acid, respectively. Unfortunately, ethanol cannot be detected due to the sensitivity of our analyses, but also due to its reactivity towards hydroxyl radicals. Ethanol behaves as a scavenger of hydroxyl radicals [27]. The pathways were evaluated based on the detection of acetic acid and pyruvic acid.

Regardless of which TiO$_2$ sample is used, the main product detected in the aqueous phase and in the presence of H$_2$O$_2$ is acetic acid (Figure 6b). In the absence of H$_2$O$_2$, acetic acid is not initially present for anatase and anatase-containing samples, but is observed in the majority of rutile samples (Figure 6a).

![Figure 6](image.png)

**Figure 6.** Acetic acid yield as a function of lactic acid conversion (a) without H$_2$O$_2$ and (b) with H$_2$O$_2$ in the presence of various catalysts. Dotted line corresponds to 100% of selectivity.

In the presence of H$_2$O$_2$, the acetic acid yield is lower for anatase than for samples containing rutile. These results agree with the formation of HO$_2^*$, which is less active than OH$^*$. It is also interesting to note that pyruvic acid formed from the initial dehydrogenation of OH groups appears
after about 60% LA conversion for all of the catalysts, except for the two commercial rutile samples where it is detected before 60% (Figure 7a). Its detection is attributed to the partial decomposition of H₂O₂, allowing for the direct adsorption of LA and immediate photocatalytic degradation. In fact, more than half of the H₂O₂ is degraded on a majority of the catalysts, and about 30% is degraded for P25 and P90 samples (Figure 7b).

![Figure 7. Pyruvic acid concentration as a function of lactic acid conversion (a) and of H₂O₂ conversion (b).](image)

In the presence of H₂O₂, the absence of pyruvic acid at low LA conversion and the high formation of acetic acid supports the hypothesis that lactic acid undergoes rapid decarboxylation upon the generation of OH° radicals.

### 2.4. Visible Photocatalytic Efficiency of TiO₂ Rutile and P25 in Presence of H₂O₂

Previously, our results showed that the photocatalytic degradation of LA and formic acid (FA) upon irradiation and in the presence of H₂O₂ and TiO₂ is correlated to the decomposition of H₂O₂. As the H₂O₂ peroxo-complex also absorbs light in the visible region, we tested the degradation of FA and LA using a rutile TiO₂ sample and visible irradiation.
Prior to investigating the impact of H₂O₂ on the photocatalytic degradation of the pollutant under visible light, a control experiment was carried out in the absence of H₂O₂. It is clear that degradation is non-negligible in the presence of rutile TiO₂ (Figure 8). These results are consistent with the visible absorption of rutile TiO₂ (absorbance drops off past 413 nm).

**Figure 8.** Degradation of FA and H₂O₂ (a) and LA and H₂O₂ (b) as a function of time in the presence of C-R100.

In the presence of H₂O₂, a significant enhancement in the degradation of FA and LA was observed, which was found to correlate directly with the decomposition of H₂O₂ (Figure 8a,b). Moreover, the disappearance rates of FA and LA are the same (6.7 µmol/L/min) with an H₂O₂ disappearance rate of about 28 µmol/L/min. In the case of FA, decarboxylation can occur, whereas with LA, both dehydrogenation and decarboxylation can occur [28]. To track their formation, we studied the intermediate products generated from LA under visible light irradiation. As shown in Figure 9a, in the presence of H₂O₂, only acetic acid was detected using visible light irradiation. This indicates that only decarboxylation occurs, which explains the comparable degradation rates for LA and FA.
Figure 9. Carbon balance of the degradation of LA in the presence (a) and the absence (b) of H$_2$O$_2$, including the formation of acetic acid and pyruvic acid and the degradation of LA.

In the absence of H$_2$O$_2$ and under visible light exposure, the first step is likely to be dehydrogenation to form pyruvic acid (Figure 9b). A similar behavior has been observed in the presence of rutile under UV irradiation [28].

Comparing to the efficiency observed under UV sources, the photocatalytic efficiency under visible irradiation is lower, about seven times smaller than the photocatalytic efficiency observed under UV irradiation at 365 nm. This difference is due to lower absorption of the H$_2$O$_2$ complex formed on the surface of the catalyst above 400 nm compared to its absorption under UV but also to the number of photons emitted by these two irradiation sources, about $4.6 \times 10^{15}$ photons/s/cm$^2$ under visible light and 7.3 photons/s/cm$^2$ under UV light. Concerning the degradation mechanism under UV and visible light, in both cases, it is due to the decomposition of the H$_2$O$_2$ complex confirmed by the similar ratio of 4–5 observed between the degradation of organic pollutant and H$_2$O$_2$ decomposition and to the main formation of acetic acid under these two irradiation sources.

The efficiency of TiO$_2$ under visible light in the presence of H$_2$O$_2$ has already been mentioned by several authors studying different molecules (terebutylazine [15], Linuron [18], Prometryn [19],...
salicylic acid [20] and decene [21]). Li et al. [20] propose a mechanism involving photoinduced electron transfer from the surface complexes of Ti(IV)–OOH. Ohno et al. [21] considered the possibility of a photochemical reaction involving TiO$_2$− peroxide. Tang et al. [15] suggests that in the presence of rutile TiO$_2$ the reaction occurs in the solution, while in the presence of anatase phase, heterogeneous reactions occur. Rao et al. [18] also showed that the demethoxylation and demethylation of linuron are the main reactions, and dechlorination and hydroxylation are only minor reactions.

In our conditions, we showed that decarboxylation is the major reaction pathway, favored over dehydrogenation.

3. Materials and Methods

3.1. Chemicals

Formic acid (99%) and lactic acid (80%), for the photocatalytic degradation tests, were supplied, respectively, by Acros Organics (Geel, Belgium) and Sigma Aldrich Chemie S.A.R.L. (Saint-Quentin Fallavier, France). Pyruvic acid (100%) and acetic acid (99.7%), intermediate products formed in the degradation of lactic acid, were supplied by Sigma Aldrich Chemie S.A.R.L. H$_2$O$_2$ (50%) was purchased from Acros Organics. Ultrapure water (18 MΩ·cm$^{-1}$) was used throughout all of the experiments.

3.2. Catalysts

Eleven titanium dioxide samples were used: two commercial TiO$_2$ samples composed of 80% anatase and 20% rutile (TiO$_2$ P-25 and TiO$_2$ P-90) from Evonik, Essen, Nordrhein-Westfalen, two commercial anatase structures (PC105 and PC-500) from Millennium Chemicals (Hunt-Valley, MD, USA), and one (Hombikat UV100) purchased from Sachtleben Chemie GmbH (Duisburg, Germany), two commercial rutile structures (MPT-625 or C-R100, and C-R160) from Ishihara Sangyo Kaisha Ldt (Osaka, Japan) and Nanostructured, respectively, and four home-made TiO$_2$ rutile catalysts synthesized from TiCl$_4$ and hydrolyzed for either 2 h or 48 h. The non-calcined samples were named HM-R2 and HM-R48, and the calcined samples were named HM-R2c and HM-R48c. A detailed description of these photocatalysts was given in our previous work [28].

The characterizations of these catalysts are given in Table 1.

Table 1. Structure, surface area, Iso Electric Point (IEP) and crystallite size of each photocatalyst.

<table>
<thead>
<tr>
<th>Photo-Catalysts</th>
<th>Structure</th>
<th>$S_{BET}$ (m$^2$·g$^{-1}$)</th>
<th>Crystallite Size (nm)</th>
<th>IEP</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25</td>
<td>80% Anatase, 20% Rutile</td>
<td>50</td>
<td>21–30</td>
<td>7–6.4</td>
<td>[29,30]</td>
</tr>
<tr>
<td>P90</td>
<td>80% Anatase, 20% Rutile</td>
<td>90</td>
<td>14</td>
<td>7–6.6</td>
<td>[29,30]</td>
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<td>PC 105</td>
<td>100% Anatase</td>
<td>88</td>
<td>15–25</td>
<td>4.7+/-0.5</td>
<td>[28]</td>
</tr>
<tr>
<td>PC 500</td>
<td>100% Anatase</td>
<td>340</td>
<td>5–10</td>
<td>6.2</td>
<td>[29]</td>
</tr>
<tr>
<td>UV 100</td>
<td>100% Anatase</td>
<td>300</td>
<td>&lt;10</td>
<td>5.3</td>
<td>[30]</td>
</tr>
<tr>
<td>C-R100 (MPT 625)</td>
<td>100% Rutile</td>
<td>103</td>
<td>13</td>
<td>5.4+/-0.5</td>
<td>[28]</td>
</tr>
<tr>
<td>C-R160</td>
<td>100% Rutile</td>
<td>160</td>
<td>8–10</td>
<td>5.1+/-0.5</td>
<td>[28]</td>
</tr>
<tr>
<td>HM-R2</td>
<td>100% Rutile</td>
<td>173</td>
<td>7.5</td>
<td>4.3</td>
<td>[28]</td>
</tr>
<tr>
<td>HM-R2c</td>
<td>100% Rutile</td>
<td>112</td>
<td>9.9</td>
<td>3.5</td>
<td>[28]</td>
</tr>
<tr>
<td>HM-R48</td>
<td>100% Rutile</td>
<td>117</td>
<td>10.5</td>
<td>4.4</td>
<td>[28]</td>
</tr>
<tr>
<td>HM-R48c</td>
<td>100% Rutile</td>
<td>92</td>
<td>12.8</td>
<td>3.6</td>
<td>[28]</td>
</tr>
</tbody>
</table>

3.3. Photocatalytic Experiments and Analytical Procedures

The photocatalytic experiments were conducted using an aqueous solution of about 1000 µM lactic acid (LA) or formic acid (FA) and 5000 µM H$_2$O$_2$. The reactions were carried out in Pyrex photoreactors. For all degradation experiments, 1 g·L$^{-1}$ of photocatalyst was used. A PLL18W Philips lamp and an HPK 125 W mercury lamp (Koninklijke Philips N.V., Amsterdam, The Netherlands) with
a filter cutting all wavelengths above 340 nm were used for the LA and FA experiments, respectively. In all cases, the UV irradiation was centered at 365 nm. A white LED emitting from 400 to 880 nm was used for visible irradiation. Prior to UV irradiation, the catalyst suspensions were allowed to reach adsorption equilibrium by stirring in the dark for 1 h. Samples of the reaction solution were taken periodically for several hours during UV or visible irradiation, filtered on a DURAPORE 0.45 µm hydrophilic membrane (Merck Millipore, Burlington, MA, USA) to remove the photocatalyst, and used for further analysis.

3.4. Analytical Procedure

H$_2$O$_2$ was complexed with an acidic solution of TiCl$_4$. Then, the H$_2$O$_2$ content of each sample was monitored at 410 nm by performing UV–vis spectroscopy in order to detect the yellow complex which forms under acidic conditions in the presence of Ti$^{4+}$ ions [31,32].

The samples were analyzed with a Shimadzu (Shimadzu Corporation, Kyoto, Japan) High Performance Liquid Chromatograph (HPLC) equipped with a Coregel-87H3 column (300 mm × 7.8 mm—Concise Separations) thermo-stated at 30 °C. A H$_2$SO$_4$ ($5 \times 10^{-3}$ mol·L$^{-1}$) mobile phase was used at a flow rate of 0.7 mL·min$^{-1}$. A diode array detector was used and set at 210 nm.

4. Conclusions

When studying the impact of H$_2$O$_2$, we found that utilizing it in combination with rutile TiO$_2$ greatly favors the oxidation of FA and LA. No additional improvement was observed in the presence of anatase TiO$_2$ under the same conditions. The higher the amount of rutile in the TiO$_2$ photocatalyst, the more significant the improvement.

By using 11 commercial and home-made TiO$_2$ samples to study the degradation of LA, we also showed that the improvement depends on the surface area of TiO$_2$. Opposing our results observed in the absence of H$_2$O$_2$, an increase in the surface area is harmful to the degradation. However, regardless of which TiO$_2$ sample is used, the degradation of LA is always correlated to the decomposition of H$_2$O$_2$.

The larger the surface area, the less lactic acid is degraded in the presence of H$_2$O$_2$. While the impact is significant in the rutile phase, in the presence of pure anatase or anatase mixed with 20% rutile TiO$_2$, an increase in surface area has much less of an impact. This behavior could be explained by an increase in the deactivation of ROS on the surface of TiO$_2$ with increasing surface area. The varying degrees of deactivation on anatase and rutile phases are potentially due to the different active species generated. On rutile TiO$_2$, OH$^\circ$ is generated by the decomposition of peroxo-complexes. It can then react with H$_2$O$_2$ forming HO$_2^\circ$, a less active species in comparison to OH$^\circ$. While HO$_2^\circ$, which is generated in the anatase phase, can react with H$_2$O$_2$ to form OH$^\circ$, this limits the negative impact of the surface area.

Our work also highlights a modification in the chemical pathways of LA in the presence of H$_2$O$_2$. Regardless of which TiO$_2$ sample is used, the formation of acetic acid was favored suggesting a promotion of the decarboxylation reaction over the dehydrogenation reaction.

Our investigation into the performance of H$_2$O$_2$ on rutile TiO$_2$ exposed to visible irradiation indicates that, for both UV and visible light, the mechanism of H$_2$O$_2$/TiO$_2$ light-driven photocatalysis is ascribed to the chemisorption of H$_2$O$_2$ on the surface of TiO$_2$ and the subsequent formation of a yellow surface complex, which is decomposed into ROSs. This mechanism is confirmed by the existence of a strong correlation between the decomposition of H$_2$O$_2$ and degradation of LA/FA under visible and UV irradiation. Moreover, we highlight that the photocatalytic degradation rates of FA and LA under visible light are identical, indicating that the decarboxylation reaction is the main pathway in the degradation of LA under visible light. This is also in agreement with our observation of acetic acid formation alone, whereas in the absence of H$_2$O$_2$, the first step is likely dehydrogenation.

These studies show that visible light, and consequently, solar light, can be efficiently used for removing some organic pollutants by photocatalysis in the presence of H$_2$O$_2$, and also by utilizing
rutile TiO₂. It could potentially also be applicable for valorization reactions. In the future, it will be insightful to investigate the degradation of different families of molecules and their chemical pathways under visible and/or UV irradiation.

**Author Contributions:** A.H. and M.H. performed the lactic acid experiments and participate to the redaction of the publication. K.S. and F.D. performed the formic acid experiments. F.D. developed the analyses of H₂O₂, lactic acid, pyruvic acid and acetic acid. C.G. designed the experiments and complemented the writing and interpretations made by A.H. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

**References**


25. Huang, W.F.; Raghunath, P.; Lin, M.C. Computational study on the reactions of H$_2$O$_2$ on TiO$_2$ anatase (101) and rutile (110) surfaces. *J. Comp. Chem.* 2010, 32, 1065–1081. [CrossRef] [PubMed]


