



Does water in synthesized TiO₂ have an effect on the photocatalytic activity? Towards a spectacular response



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ABSTRACT

The influence of hydroxyl radicals on the photocatalytic performance of synthesized TiO₂ resulting from the addition of water was studied. Two TiO₂ samples were prepared using the sol-gel method followed by calcination at 600 °C. The aim of this work was to study the effect of water on the photocatalytic activity of a model compound – formic acid (FA) – by comparing between the titanium oxide synthesized with water (TiO₂-600-w) and without water (TiO₂-600). The TiO₂-600-w, consisting of anatase and a little rutile, was the most active catalyst, whereas pure anatase (in case of TiO₂-600), showed low photocatalytic efficiency. In this study, we confirmed that the filling of the TiO₂ surface by hydroxyl radicals could produce better photocatalytic activity by reducing e⁻/h⁺ recombination. It is notable, however, that with TiO₂-600-w, the degradation rate (found under UV) was about 4–5 times greater than that obtained with TiO₂-600. This result suggests that the presence of water was very important in the synthesis of TiO₂ and brought a dramatic gain in the photocatalytic response as well.

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1. Introduction

Photocatalysis quantitatively represents an efficient method for producing radicals, and in particular hydroxyl radicals. The hydroxyl radical can be categorically considered as a water molecule fragment. Being a particularly stable molecule, the fragmentation of water necessitates the a priori contribution of an important energy.

Titanium dioxide (TiO₂) is the most commonly used catalyst in photo-induced reactions, mainly because of its chemical stability and high photocatalytic activity. On its surface, the irradiation of the catalyst causes the decomposition of water into ·OH radicals that are able to degrade the organic pollutants until complete mineralization [1,2].

The interaction of water with the TiO₂ surface is an important research topic since it plays a major role, especially in photocatalysis [3]. Very few authors, however, have been interested in the effect of the adsorption state of the nanocrystal surfaces on their structure [4] and few studies are concerned with the moisture content during the synthesis of TiO₂ [5]. Previous studies concluded that the improvement in the photocatalytic activity is due to a bet-

ter separation of electron-hole pairs yet they lacked precision [6,7]. Current studies, by contrast, often lack correlation between the properties of water and the photocatalytic performance of TiO₂ [8]. This work made it possible to better understand the surface reactivity of TiO₂ nanoparticles synthesized with and without water and its photocatalytic role through the degradation of formic acid. The formic acid was chosen here because its photodegradation could be conducted both by direct hole transfer and by photo-generated surface radicals [9]. The photocatalytic activities of both TiO₂-600-w and TiO₂-600 samples were then studied and compared with the high activity of the reference TiO₂ P25.

2. Experiment

The precursor used for the synthesis of TiO₂ was titanium tetrachloride (TiCl₄) (99.99%) purchased from Sigma Aldrich. The solvent, absolute ethanol, (≥99.99%) was bought from Merck Millipore (Germany). The reagents and the model pollutant (HCOOH) were obtained from Acros Organics and were used without any further purification. Two samples of TiO₂ were prepared by the sol-gel method described as follows: an amount of TiCl₄ was slowly added to 10 ml of absolute ethanol. During the synthesis, an amount of water (volumetric ratio of water/TiCl₄ = 1/3) was only added to one sample of TiO₂. In this catalyst (TiO₂-600-w),

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(w) indicates the presence of water. Next, the solution obtained with and without water converted into a colorless solution that produced TiO₂ nanopowders through the drying process at 85 °C in an oven for 15 h. The obtained TiO₂ nanopowders were eventually calcined in an oven for 2 h at a temperature of 600 °C. X-ray diffraction analyses (XRD) were carried out using a X'Pert Pro Panalytical diffractometer with Cu K α radiation ($\lambda = 1.54184$ Å). The material to be tested was introduced into a photo-reactor containing 30 ml of the solution of the pollutant whose initial concentration was 50 ppm of formic acid. The solution was stirred in the dark for 60 min to reach the adsorption equilibrium at the catalyst surface. The samples were, then, irradiated and aliquots were taken every 5 min and filtered later through Millipore filters (porosity 0.45 μ m). Next, they were analyzed using a high performance liquid chromatography (HPLC).

3. Results and discussion

3.1. Structural and morphological properties

Fig. 1 shows the XRD spectra of pure TiO₂ nanopowders with and without water. The obtained results show that the presence of water has influenced the composition of the TiO₂ powders and the crystallization phase and that, due to the presence of water during the synthesis, the anatase phase has been modified a bit into a rutile. The phase transition was accompanied by crystal growth. Table 1 summarizes the percentages of anatase and rutile in both samples. The crystallite size of TiO₂ nanoparticles was determined based on the Scherrer equation. In fact, anatase TiO₂ is considered as the most efficient catalyst [10]. The presence of a small amount of rutile, however, seems to improve the effectiveness of anatase TiO₂. Despite the fact that this improvement is still a subject of much debate, most publications have mentioned that the source of their effectiveness could be attributed to an interface between anatase and rutile [11,12]. Measurements in infrared (FT-IR) spectroscopy were carried out so as to determine the surface reactivity and, more precisely, the surface charge which could immediately influence the adsorption properties. In Fig. 2, we can observe clear changes between the two spectra of TiO₂ with and without water in the band intensity, especially a broad band observed between 3100 cm⁻¹ and 3400 cm⁻¹ in the spectrum of TiO₂-600-w and which disappeared in the spectrum of TiO₂-600.

Table 1

Percentages of the crystalline phase of different samples and degradation rate of TiO₂-600-w, TiO₂-600, P25. A and R denote anatase and rutile, respectively.

Samples	Phase content (%)	r_0 (μ mol/L/min)
P25	A: 80; R: 20	26.74
TiO ₂ -600	A: 100	17.16
TiO ₂ -600-w	A: 96; R: 4	71.93

This band could be caused by the presence of hydroxyl groups –OH adsorbed on the surface which came from the water added during the synthesis and which were gradually released and strongly linked to the TiO₂ surface.

3.2. Evaluation of photocatalytic activities of the TiO₂ samples

3.2.1. Impact of water on the adsorption of FA

Fig. 3a displays the adsorbed amounts of formic acid on the three photocatalysts TiO₂-600-w, TiO₂-600 and TiO₂-P25. If we go through Fig. 3a, we can notice that after 60 min in the dark, a slight adsorption of formic acid on each type of oxide samples was observed: 10% for TiO₂-600-w, 6% for TiO₂-600 and 8% for TiO₂-P25. A large number of parameters could have influenced the adsorption of formic acid on the surface of TiO₂ such as surface hydration and adsorption mechanisms [13]. The adsorption of formic acid was due to the hydrogen bond between the oxygen of the carboxylic group on the acid and the hydroxyl groups of TiO₂.

3.2.2. Impact of water on the disappearance of FA

Fig. 3b shows the kinetics of formic acid in the presence of TiO₂-600-w, TiO₂-600 and TiO₂-P25 under exposure to UV-A radiation. The comparison between titanium oxide with and without water shows a beneficial influence of water and a distinct increase in the photocatalytic response. The presence of a larger amount of water in the synthesis of TiO₂-600-w than that of TiO₂-600 was able to overload the catalyst surface with active radicals. This, then, could explain the systematic activity of the greater degradation of TiO₂-600-w. The results shown in Table 1 clearly demonstrate the important photocatalytic role of water. The degradation rate with TiO₂-600-w is about 4 or 5 times greater than with TiO₂-600. The improvement in velocity is also explained by the production of ·OH which very often came with the appearance of other chemical

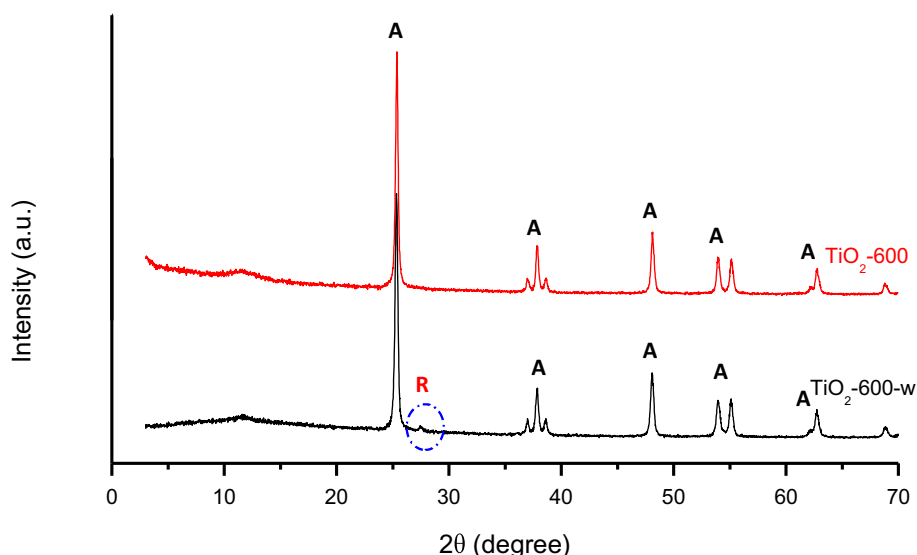


Fig. 1. XRD patterns of TiO₂-600-w and TiO₂-600 nanomaterials. (A: anatase, R: rutile).

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