Acid acting as redispersing agent to form stable colloids from photoactive crystalline aqueous sol-gel TiO₂ powder

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Abstract

In this work, the redispersion of three nanocrystalline TiO₂ colloids is studied: one pure and two Fe-doped titania. These three colloids are produced by an easy aqueous sol-gel synthesis using precipitation-acidic peptization of Ti precursor. For the two Fe-doped TiO₂, one is doped during synthesis (primary doping) and the other is doped after the synthesis (secondary doping). The initial colloids are composed of crystalline TiO₂ particles around 7 nm with good

photocatalytic properties, tested on PNP degradation under visible light (wavelength > 390 nm).

The powders obtained by air drying of these three colloids are redispersed in water to produce colloids which are compared to the initial colloid produced. For each colloid, 5 cycles of drying-redispersion are achieved. The colloids are characterized by dynamic light scattering, zeta potential measurements, inductively coupled plasma–atomic emission spectroscopy, X-ray diffraction, nitrogen adsorption-desorption measurements, Mössbauer spectroscopy, diffuse reflectance spectroscopy, and photocatalytic tests. The results show that similar products are obtained between the cycles, maintaining homologous properties of colloids. This property of redispersion is mainly due to the acid (HNO_3, HCl, or H_2SO_4) which protonates the surface of the TiO_2 nanoparticle leading to high surface charges and electrostatic repulsions between aggregates. This property can be very useful for industrial applications of this synthesis, especially as it allows the volume and weight to be reduced for transportation and storage. Moreover, results show that the pure TiO_2 powder can be doped during its redispersion step. The redispersion of the TiO_2 developed here is possible without surface functionalization or multiple step processes, contrary to commercial Degussa P25. A two year stability study of all the produced colloids has been performed by following the evolution of the macroscopic aspect and the physico-chemical properties of these sols. This study showed high stability of the produced colloids.

Keywords: Aqueous TiO_2 sol-gel synthesis, redispersion property, photocatalysis, recycling, Fe-doping, colloid stability

Highlights

- Crystalline TiO_2 colloids synthesized by aqueous sol-gel method
- Redispersion cycles of the TiO_2 dried powder are studied

- Physico-chemical and photocatalytic properties are maintained through redispersion

- Acid plays the main role as the redispersing agent of the crystalline powder

- Redispersion allows reduction of the volume and weight for transportation and storage

1. Introduction

For decades photocatalysis has been widely studied in a large range of applications, such as water and air depollution [1], anti-fogging and easy-to-clean coatings [2,3], dye sensitization, and solar energy conversion [4–6]. Among the different photocatalysts, TiO_2 is the most used material [7] because of its high oxidative potential, chemical stability, availability, and relatively low price [1]. The amount of energy required to activate TiO_2 is equal to 3.2 eV for anatase phase, which corresponds to the energy of ultra-violet light (at least 388 nm). So, if natural light is used for activation, only 5-8% of the solar spectrum is useful [8].

When TiO_2 is illuminated by sufficiently energetic light, electrons (e^-) are promoted from the valence band to the conduction band leading to the formation of positive holes (h^+) in the valence band. When these photo-generated e^- and h^+ are at the surface of the catalyst, they produce radical species such as $O_2^-\bullet$ (superoxide) and $^\bullet OH$ from reactions with adsorbed O_2 and H_2O. These radicals react with the pollutant adsorbed on the surface of TiO_2 and induce pollutant degradation [3,7,9].

The TiO_2 superhydrophilicity is mainly due to photogenerated holes. These holes can induce the appearance of oxygen vacancies which promote the adsorption of water and so the formation of superficial –OH groups [2]. These hydroxyl groups have a high affinity with water promoting the formation of a water film characterized by a low contact angle (< 10°) [2,10,11].

Sol-gel synthesis has proven to be effective for the synthesis of TiO_2 with control of the nanostructure and surface properties in "soft conditions", *i.e.* low pressure and temperature [12–16]. With this process, it is possible to produce crystalline TiO_2 at temperatures below 100°C and without calcination [3,8,17–20].

Depending on the application, TiO_2 can be used as a powder or film. For example, for water treatment TiO_2 powder can be mixed with the polluted water and, after illumination, it can be filtered to recover clear water [8,18]. The main advantages of powder catalysts are that the contact with pollutant is good and can be easily increased by adding catalyst, additionally, it is easy to transport the powder to where it is used. Nevertheless, the depolluted water needs to be filtered to recover the catalyst. To obtain a functionalized surface of TiO_2, a film can be deposited on glass or steel to produce a photocatalytic [21,22] or self-cleaning [2,3] surface using different deposition techniques like dip-coating, bar-coating, spin-coating, or spray-coating with a stable TiO_2 colloid. In this case, the catalyst is supported on a substrate which is easily removed from the depolluted water. However, to produce a TiO_2 film using a sol-gel technique, it is necessary to use a stable TiO_2 colloid to ensure a homogenous film. The transport of this liquid for its deposition can be difficult and dangerous due to the large volume of chemicals required. The liquid colloid needs to be stable, which means it keeps its properties over a large period of time and does not precipitate. A TiO_2 colloid that can be obtained by a simple redispersion of a catalyst powder in a solvent would be very useful.

In previous studies an aqueous TiO_2 synthesis was developed, producing stable nano-colloids of crystalline pure [3] and doped [18] TiO_2. These syntheses were extrapolated towards a larger scale, up to a volume of 5 L. Pure TiO_2 material was used to produce films deposited on steel at a large scale, in order to produce an easy-to-clean surface [3]. Doped TiO_2 powders produced with this eco-friendly synthesis [18,23] were tested for water depollution and showed higher photocatalytic values than the commercial photocatalyst Degussa P25.

The main goal of this work is to show the redispersion properties of pure and doped TiO_2 colloids synthesized by the aqueous sol-gel process and its interest for further applications. The powders obtained by drying these colloids can be redispersed easily in water forming a homologous colloid identical to the initial one. This redispersion property has never been studied before. The major element in the redispersion phenomenon is identified and its role in the initial synthesis is described. To reach this goal, one pure and two Fe-doped TiO_2 samples (primary and secondary doping) are studied.

For each sample, 5 cycles of redispersion-drying are achieved. After each cycle, the colloid and the dried powder are characterized by dynamic light scattering, zeta potential measurement, nitrogen adsorption-desorption measurements, X-ray diffraction, Mössbauer spectroscopy, diffuse reflectance spectroscopy, photocatalytic activity tests, and compared to the initial material. For the first time on a TiO_2 sol-gel colloid, a long time stability study is made of the colloids over two years, where every six months the colloids undergo a series of characterizations to assess the stability of their properties and the impact of storage.

Fe-doping during the redispersion step is also tested on pure TiO_2 initial powder in order to compare this secondary doping with Fe-doping done during synthesis (primary doping).

A comparison with commercial Degussa P25 is made.

2. Materials and methods

2.1. Sample preparation

2.1.1. Pure TiO_2 powder synthesis

Titanium (IV) tetraisopropoxide (TTIP, > 97%, Sigma-Aldrich), nitric acid (HNO_3, 65%, Merck), isopropanol (IsoP, 99.5%, Acros), and distilled water are used as starting materials. Pure TiO_2 is synthesized according to [3], using water as the solvent and nitric acid for TTIP peptization. After 4 h, a light blue transparent liquid sol is obtained. The sol is dried under an ambient air flow to obtain a xerogel, which is crushed to a white-yellow powder [3]. The pure TiO_2 sample is denoted as "TiO_2".

An alternative synthesis of pure TiO_2 is also tested. In this case, TTIP + IsoP are precipitated in water without nitric acid and dried. This powder is then mixed in water with HNO_3 ($pH = 1$) at 80°C for 4 h. After 4 h, a light blue transparent liquid sol is obtained. The sol is dried under an ambient air flow to obtain a xerogel which is crushed to a white-yellow powder [3]. This pure TiO_2 sample is denoted as "TiO_2 bis".

2.1.2. Fe-doped TiO_2 powder synthesis

The TiO_2 catalyst is doped with Fe^{3+} metallic ions from the corresponding nitrate salt (iron (III) nitrate nonahydrate, Sigma Aldrich ACS reagent, $\geq$ 98%) according to [18], also using water as the solvent and nitric acid for TTIP peptization. After the reaction time, a light blue-orange transparent liquid sol is obtained. As for the pure TiO_2 sample, the doped TiO_2 catalyst is dried under ambient air and crushed to obtain a pale-orange powder. The Fe-doped TiO_2 sample is denoted as "TiO_2/Fe0.5", where 0.5 is the molar percentage of iron in the sample.

2.1.3. Fe-doping of the redispersed pure TiO_2 (secondary doping)

For this, 3.3 g of pure TiO_2 is mixed in 73 mL of deionized water containing 0.068 g of iron (III) nitrate nonahydrate. The mixture is ultra-sonicated for 30 min, the sol is then stirred for 4 h at 80°C. A light blue-orange transparent liquid sol is obtained. As for other catalysts, the sol is dried under ambient air and crushed to obtain a pale-orange powder. Redispersed TiO_2 samples doped with Fe are denoted as "TiO_2+Fe0.5", where 0.5 is the molar percentage of iron in the sample.

2.1.4. Catalyst redispersion

In this study, all TiO_2 powders are redispersed by mixing 6.3 g of the powder in 200 mL of deionized water, and the mixture is ultra-sonicated for 30 min. A transparent liquid sol is obtained and can be dried under ambient air and crushed to obtain powder. Redispersed samples are denoted as "sample name-RX", where X is the number of redispersion-drying steps achieved on the sample. Both pure and Fe-doped TiO_2 samples are redispersed 5 times producing 10 redispersed samples.

The same protocol of redispersion is also tested on the commercial Degussa P25 photocatalyst.

2.2. Sample characterization

In the sol, the sizes of TiO_2 aggregates are estimated by dynamic light scattering (DLS) in a DelsaNano C device from Beckman Coulter. This measurement gives a hydrodynamic diameter of aggregates [24].

The zeta potential and particle mobility, μ_p, are measured on the different sols with a DelsaNano C device from Beckman Coulter, giving information about colloid stability.

The actual amount of iron in the Fe-TiO_2 sample is evaluated by inductively coupled plasma–atomic emission spectroscopy (ICP-AES) on a VARIAN Liberty Serie II device. The samples undergo an alkaline fusion, the following steps are made: 0.2 g of Na-KCO_3, 2 g of Na_2O_2, and 0.2 g of sample are mixed together in a zirconium crucible. Then the mixture is heated to its melting point; after cooling and solidification of the mixture, the crucible is placed in a 500 mL flask with deionized water. After reaction, the crucible is removed from the flask and 6 mL of HNO_3 is added. The mixture is heated to its boiling point for 5 min then the solution is transferred to a volumetric flask that is filled to the calibration mark with deionized water after cooling. The solution is then analyzed using an ICP-AES device.

The crystallographic properties are studied through the X-ray diffraction (XRD) patterns recorded with a Bruker D8 Twin-Twin powder diffractometer using Cu-K_α radiation. The Scherrer formula (Eq. 1.) is used to determine the size of the TiO_2 crystallites, d_{XRD} [25]:

$$d_{XRD} = 0.9 \frac{\lambda}{(B \cos(\theta))}$$

(1)

where d_{XRD} is the crystallite size (nm), B the peak full-width at half maximum after correction of the instrumental broadening (rad), λ the wavelength (nm), and θ the Bragg angle (rad).

The repartition of the crystallographic phases is estimated with the Rietveld method using *"Profex"* software [26]. The amount of crystalline phase is estimated with CaF_2 internal

standard (calcium fluoride, Sigma-Aldrich, anhydrous powder, 99.99% trace metal basis) also using *"Profex"* software [27].

The sizes of TiO$_2$ nanoparticles are estimated by transmission electron microscopy (TEM) by averaging the measurement of approximately 100 particles on TEM micrographs obtained with a Phillips CM 100 device (accelerating voltage 200 kV). First, samples are dispersed in distilled water using an ultrasonic treatment. Then a drop of the dispersion is placed on a copper grid (Formvar/Carbon 200 Mesh Cu from Agar Scientific).

The TiO$_2$ textural properties are characterized by nitrogen adsorption-desorption isotherms in an ASAP 2420 multi-sampler adsorption-desorption volumetric device from Micromeritics. From these isotherms, the microporous volume is calculated using Dubinin-Radushkevich theory (V_{DR}). The surface area is evaluated using Brunauer, Emmett, and Teller theory (S_{BET}) [28]. An average particle size, d_{BET}, can be calculated from S_{BET} values by assuming spherical and non-porous TiO$_2$ anatase nanoparticles using the following formula [8]:

$$\frac{d_{BET}}{6} = \frac{\dfrac{1}{\rho_{anatase}}}{S_{BET}} \tag{2}$$

where $\rho_{anatase}$ is the apparent density of TiO$_2$-anatase estimated to be equal to 3.89×10^6 g m^{-3} [3, 8].

The sample's optical properties are evaluated by diffuse reflectance spectroscopy measurements in the 300–800 nm region, using a Varian Cary 500 UV–Vis-NIR spectrophotometer equipped with an integrating sphere (Varian External DRA-2500), and using BaSO$_4$ as reference. The UV–Vis spectra recorded in diffuse reflectance (R_{sample}) mode are transformed by using the Kubelka–Munk function:

$$F(R_\infty) = \frac{(1-R_\infty)^2}{2R_\infty} \tag{3}$$

where R_∞ is defined as $R_\infty = R_{sample}/R_{reference}$ [8,29,30] with $R_{reference}$, the diffuse reflectance measured for the BaSO$_4$ reference. For comparisons, all spectra are normalized to 1.0 by dividing each spectrum by its maximum intensity [8,31]. Using the well-known equation:

$$(F(R_\infty)h\nu)^{1/m} = C(h\nu - E_g) \tag{4}$$

where C is a constant and m is a constant which depends on the optical transition mode, the direct and indirect optical band-gap values, $E_{g,direct}$ (eV) and $E_{g,indirect}$ (eV), are obtained by plotting, respectively, $(F(R_\infty)h\nu)^2$ and $(F(R_\infty)h\nu)^{1/2}$ as a function of the photon energy $h\nu$ and by determining the intersection of the linear part of the curve and the x-axis [8,32].

Mössbauer spectra were obtained on a constant acceleration spectrometer at 295 K with a cobalt-57 source calibrated with α-iron foil. As iron contents in the samples are very low, the measurement time is high (2 weeks for each sample) and only TiO$_2$/Fe0.5, TiO$_2$/Fe0.5-R5, TiO$_2$+Fe0.5, and TiO$_2$+Fe0.5-R5 samples were measured.

2.3. Photocatalytic tests

The photocatalytic activity of the samples in powder form is evaluated by following the degradation of *p*-nitrophenol (PNP) after 24 h (D_{PNP24}) under a halogen light covered by a UV-filter which removes wavelengths lower than 390 nm: this condition is called low energy light [18]. The experimental step-up is shown in [8,33]. The concentration of PNP is measured by UV/Vis spectroscopy (GENESYS 10S UV–Vis from Thermo Scientific) at 318 nm. For each catalyst, three flasks are exposed to light to calculate the PNP degradation and one is kept in the dark (dark test) to evaluate PNP adsorption on samples. Additionally, a flask with only PNP is exposed to the light for 24 h (blank test) to evaluate natural PNP decomposition under visible

light. In each flask the initial concentrations of catalyst and PNP are 1 g L^{-1} and 10^{-4} M, respectively. Experiments are conducted in test tubes fitted with a sealing cap. These tubes are placed in a cylindrical glass reactor with a halogen lamp in the center. The halogen lamp has a continuous spectrum from 390 to 800 nm (300 W, 220 V), measured with a Mini-Spectrometer TM-UV/vis C10082MD from Hamamatsu. The reactor is maintained at constant temperature (20°C) by a cooling system which functions by recirculating water, the lamp is also cooled by a similar system. Aluminium foil is used to cover the outer wall of the reactor to prevent any interactions with the room lighting. Each 10 mL flask in the reactor is agitated by a magnetic stirrer. The PNP degradation due to photocatalysis is equal to the total PNP degradation minus the PNP adsorption (dark test).

2.4. Colloid stability study

The stability of the colloids and the corresponding powders is studied over two years with various characterizations. Every six months, the following measurements are made on each colloid: macroscopic observations of the sol to see if precipitates or particles are observed in the liquid, DLS measurements on DelsaNano C device from Beckman Coulter, film formation on a glass substrate by dip-coating and estimation of the produced thickness with profilometer (Veeco Dektak 8 Stylus Profile). The following measurements are made on the corresponding powder: XRD, nitrogen adsorption-desorption isotherms, and photocatalytic measurement. Through these characterizations it is possible to know if the colloid and the corresponding powder keep their properties.

The syntheses described in Sections 2.1.1. to 2.1.3. are realized in volumes of 6 L in order to have enough colloid for the stability study. After the redispersion steps (Section 2.1.4.), 1 L of

each condition are kept in a sealed flask at ambient temperature in the dark, and 19 colloids are available for the study.

3. Results

3.1. Macroscopic observations of sols and powders

For the pure TiO_2 sample, the corresponding sol is white transparent with some blue reflections and the powder is white-yellow. For the TiO_2/Fe and TiO_2+Fe samples, the corresponding sols are orange transparent with some blue reflections, and the powders are pale orange. All redispersed samples have the same aspect both for the corresponding initial sols or powders. The commercial Degussa P25 sample forms precipitates during redispersion.

For Fe-doped samples the actual Fe molar percentage, measured by ICP-AES, remains stable during the redispersion step (Table 1). The hydrodynamic diameter of TiO_2 aggregates stays constant (around 50 nm) through the redispersion (Table 1).

For each sol the zeta potential is around 30 mV (Table 1) and no precipitate is observed. The particle mobility is positive for each sample and is around 25.10^{-5} cm^2 V^{-1} s^{-1} (Table 1).

3.2. Catalyst textures and morphology

For all samples, textural properties are presented in Table 1. For each catalyst, nitrogen adsorption-desorption isotherms (Figure 1 for the pure TiO_2 sample series) are very similar, with a sharp increase at low pressure followed by a plateau which corresponds to a microporous

solid from the BDDT classification (type I isotherm) [28]. The numerous redispersion cycles and the secondary doping have no effect on textural properties as S_{BET} and V_{DR} values are similar for both pure and Fe-doped TiO$_2$ samples (Table 1). For example, S_{BET} values are equal to 200 and 190 m^2 g^{-1} for TiO$_2$ and TiO$_2$-R5, respectively. An average nanoparticle diameter (d_{BET}) can be calculated with Eq. 2, giving a size of about 7-9 nm for all samples.

TEM micrographs for some samples at different magnifications are presented in Figure 2. For all samples, TiO$_2$ aggregates are observed; these aggregates are composed of TiO$_2$ nanoparticles with spherical shapes. The particles are not perfectly separated from each other because the material was first dried and then deposited on the TEM grid for measurement; also the TiO$_2$ nanoparticles are not very clearly observable by TEM because of their relatively low contrast in bright-field TEM conditions [18]. All samples (initial and redispersed) have the same aspect. TiO$_2$ nanoparticles have a size of about 5-7 nm. The TiO$_2$ average size estimated from TEM (d_{TEM}) is similar to that estimated from XRD (d_{XRD}, Table 1). No difference can be found between doped and undoped samples, so it is supposed that iron is well dispersed in the TiO$_2$ matrix.

3.3. Catalyst crystallinity

The XRD patterns for the pure TiO$_2$ sample series are shown in Figure 3. For each material the same pattern is obtained, with mainly TiO$_2$ anatase phase and a small amount of brookite (peak around 31°). The crystallite size is calculated with the Scherrer formula (Eq. 1), all samples have a size of around 5-6 nm. The numerous redispersion cycles and the secondary doping have

no effect on crystallinity of samples. The same patterns, with the same crystallite sizes, are obtained with all doped samples (not shown).

For all samples an estimation of the phase repartition is made with *Profex* software [26] and calibration CaF_2 to obtain the crystalline and amorphous fraction, all the results are depicted in Table 1. In each sol-gel material, approximately (distribution value ± 5%) the same phase repartition is observed: the anatase phase is the main crystalline phase corresponding to 65-75% of the samples, the brookite phase is around 10%, and the amorphous fraction corresponds to 15-25%. For the P25 sample, the distribution is as follows: anatase is around 80%, rutile is around 20%, and nearly no amorphous phase is observed.

3.4. Iron doping

Mössbauer spectroscopy was used in order to obtain additional information on the iron doping and any difference between the two types of doping in the studied samples. The Mössbauer spectra are shown in Figure 4 for $TiO_2/Fe0.5$-R5 and $TiO_2+Fe0.5$-R5 samples, the spectra are the same for the initial $TiO_2/Fe0.5$ and $TiO_2+Fe0.5$ samples. The spectra exhibit rather low statistics due to low iron content [18]. All spectra show the presence of paramagnetic iron, which confirms the absence of any magnetic ordering of Fe-containing TiO_2 materials at room temperature [18]. The lack of magnetic ordering also proves the absence of any supermagnetic iron oxides, hematite α-Fe_2O_3 or Fe_3O_4 magnetite, in the sample and excludes the presence of magnetic Fe clusters within the TiO_2 matrix [18]. This result confirms the successful incorporation of Fe^{3+} into the TiO_2 lattice [18].

For $TiO_2/Fe0.5$ and $TiO_2/Fe0.5$-R5 samples (Figure 4 A), two components of Fe^{3+} can be observed to fit the data: (i) the first corresponds to a high-spin trivalent iron in an FeO_6-type octahedral site in the core of the sample (green), (ii) the second one corresponds to a lower coordination of the Fe^{3+} ion site in an interstitial position within the TiO_2 structure in the shell

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of the sample (blue). Same spectrum is obtained for both TiO_2/Fe0.5 and TiO_2/Fe0.5-R5 samples. Similar observations were made previously on these types of material [18].

For TiO_2+Fe0.5 and TiO_2+Fe0.5-R5 samples (Figure 4 B), only one Fe^{3+} component (blue) is observed corresponding to a lower coordination of the Fe^{3+} ion site in an interstitial position within the TiO_2 structure in the shell of the sample as the second component of TiO_2/Fe0.5 and TiO_2/Fe0.5-R5 samples [18]. In this case, the addition of dopant after the synthesis of the TiO_2 matrix (secondary doping) only allows iron to go into the interstitial position of the TiO_2 network. The same spectrum is obtained for both TiO_2+Fe0.5 and TiO_2+Fe0.5-R5 samples.

3.5. Photocatalytic activity and optical properties

The sample activity, D_{PNP24}, is shown in Table 1 for each sample after 24 h of illumination under low energy light.

For both pure and Fe-doped TiO_2 samples, the activity is independent of the number of redispersion-drying cycles. However, in the case of Fe-doped TiO_2 the PNP degradation is higher than that of the pure sample (respectively 45% and 25% degradation of total PNP).

For the commercial Degussa P25 sample, the PNP degradation is equal to $12 \pm 3\%$, which is lower than that of the pure TiO_2 sample synthesized by the aqueous sol-gel process (Table 1).

The evolution of the normalized Kubelka–Munk function $F(R_\infty)$ with wavelength (λ) for TiO_2, TiO_2/Fe0.5, and TiO_2+Fe0.5 samples is shown in Figure 5. The samples present absorption at 360 nm and no great difference is observed between the samples. All redispersed samples (-RX samples) have the same spectrum as the reference spectrum of their series, so the curves are not shown. The direct and indirect band gaps are calculated for all samples (Table 1).

3.6. Colloid stability study

Concerning the stability of the colloids, all the measurements over time are shown in Tables 2 and 3. For the macroscopic observations, no precipitate or large particles are observed in all samples, and TiO_2 nanoparticles stay in suspension. Furthermore, the colors of the sols are the same as those described in Section 3.1. Figure 6 shows the TiO_2 sol after two years, where no precipitate is observed.

For the physico-chemical characterizations, DLS measurements confirm the macroscopic observations as the hydrodynamic diameter stays nearly constant in each case (Table 2, 6 to 24 months) and the films produced by dip-coating have the same thickness over time, so no aggregation of particles occurs. The XRD and nitrogen adsorption-desorption isotherm measurements (Table 3) show no variation in the physico-chemical properties of the corresponding powder. Moreover, the photoactivity stays constant. The materials are very stable over the two years.

4. Discussion

4.1. Role of acid in synthesis

The synthesis is based on the precipitation-peptization of a titanium precursor in excess of water, leading to the formation of a stable crystalline TiO_2 nanoparticle sol [17,34–36].

When TTIP is added to water, hydroxylated titanium precipitates are formed, then nitric acid allows the peptization of these mainly amorphous titania into crystalline TiO_2 [17]. This acid leads to a strong surface charge on the TiO_2 particles, breaking big titania aggregates by electrostatic repulsion. Moreover, acid and heat increase titania solubility in water, leading to a forced hydrolysis [17,37] of the amorphous TiO_2, followed by nucleation and crystallization of the TiO_2 nanoparticles in anatase-brookite phases. The role of the acid is to disperse and to crystallize TiO_2 nanoparticles.

In this work, two syntheses of pure TiO_2 are performed to confirm the importance of acid. The TiO_2 bis sample is synthesized in two steps, corresponding first to the precipitation of amorphous TiO_2 in pure water, and second to TiO_2 crystallization in acidic medium with heat. In the TiO_2 sample both steps take place at the same time. The two pure TiO_2 samples (TiO_2 and TiO_2 bis) have homologous properties (Table 1) showing that both syntheses lead to similar materials. Without acid, only amorphous TiO_2 precipitate is formed.

In this study, both pure TiO_2 and TiO_2/Fe0.5 samples form stable sols of anatase-brookite nanoparticles with no precipitate, even after several months of storage, and keep the same aggregate size ($D_{DLS} \sim 50$ nm, Table 2) over time.

When these materials are dried under ambient air, a redispersion in water is possible, forming a stable sol identical to the initial one (Table 1).

4.2. Redispersion

For pure TiO_2, TiO_2/Fe0.5, and TiO_2+Fe0.5 samples, five cycles of redispersion of these materials in water are achieved and characterized to study the influence of this operation on the

physico-chemical properties of TiO$_2$. Through the results (Table 1), it is observed that homologous materials are obtained between the different cycles as the macroscopic observations of powders and sols, the texture, crystallinity, photoactivity, aggregate sizes, and zeta potential are the same for all the redispersed samples.

The acidity of the solution is probably the main factor for the very good redispersion of these TiO$_2$ materials. The *pH* of the sols is equal to 1-1.3 for all the samples. Therefore, the surface of the TiO$_2$ nanoparticles is positively charged according to the following equilibrium with *pH* [38]:

$$TiOH_2^+ \underset{+H^+}{\overset{-H^+}{\longleftrightarrow}} TiOH \underset{+H^+}{\overset{-H^+}{\longleftrightarrow}} TiO^- \tag{5}$$

Moreover, the mobility measured for all samples is positive (Table 1), as this value is proportional to the surface charge of the particles [39], so the different colloids have a positive surface charge. The electrostatic repulsions between aggregates allow a stable sol to form, keeping the same aggregate sizes and zeta potentials (Table 1) through redispersion. For this type of synthesis, same values of aggregate sizes and zeta potentials are found in the literature [34,35]. Drying under ambient air leaves nitric acid at the surface and between the titania particles, which can act as a redispersing agent when this powder is added to water during the different redispersion cycles. If the powder is heated to 100°C, no stable sol is obtained when the powder is added to water, it forms precipitates and the *pH* increases to 4, which shows that the acid was removed during heating. However, when nitric acid is added to reach a *pH* of 1, a stable sol is reobtained. Other acids (HCl, H$_2$SO$_4$) have been tested for powder redispersion and also produce a stable colloid. This shows the main role of acid, which acts as a dispersing agent of TiO$_2$ nanoparticles. This property of redispersion is obtained with both pure and Fe-doped TiO$_2$ sols (Table 1). The stability study has shown that after two years of storage the samples

keep their macroscopic aspect and all their properties (crystallinity, texture, and photoactivity). This stability can be attributed to the acid which allows the high repulsion between the nanoparticles. With a quite simple phenomenon (electrostatic repulsion), it is possible to produce a colloid with photocatalytic properties that is stable for years.

4.3. Different methods of synthesis and redispersion

In Figure 7, the different ways to obtain crystalline TiO_2 colloids with homologous properties are presented. One method consists in the mixing of Ti precursor in water, and a crystalline TiO_2 colloid is obtained by adding HNO_3 with heat. A crystalline colloid can also be obtained by peptization of amorphous TiO_2 powder with HNO_3 and heat. As described in the previous paragraphs, if the crystalline colloid is dried under ambient air the resulting powder can be redispersed in water several times (Figure 7, redispersion cycle). However, if the powder is dried at 100°C, the acid is removed and a stable colloid is not obtained unless HNO_3 is added (Figure 7). Each crystalline colloid obtained in Figure 7 can be redispersed by the cycle "ambient air drying-redispersion in water" and keep their properties.

This property of redispersion can be very useful for use at a larger scale.

4.4. Type of doping

The Mössbauer spectra (Figure 4) show that there is a difference between the two methods of doping. When the doping occurs during the TiO_2 formation (TiO_2/Fe0.5 samples) some iron can be introduced into the network of TiO_2, while for the secondary doping the iron is added in

an interstitial position. Two types of doping are clearly observed: "network" doping (for the primary doping samples) and "interstitial" doping (for the secondary doping samples).

However, this difference has no great influence on the photocatalytic activity which stays nearly the same for both series of iron doped samples (Table 1). In this doping, the beneficial effect of iron on the photocatalytic property of the doped TiO_2 probably comes from a photo-Fenton effect [18]. The iron in the interstitial position is more available for the photo-Fenton mechanism than Fe^{3+} in the TiO_2 network. A secondary doping can be efficient for a photocatalytic application, but the dopant needs to be chosen with care.

4.5. Industrial application

In previous works [3], it has been shown that these materials can be synthesized at a larger scale and are used at pilot scale to coat stainless steel, giving self-cleaning properties in a pilot scale line (roll-to-roll process) which is closer to industrial scales, with a process that is cheaper than vacuum plasma deposition. The property of redispersion of these materials is an additional advantage for industrial applications of this material.

First, redispersable powders allow a weight and volume gain for transport and storage. For example, in the case of the deposition of this TiO_2 colloid on a pilot line for self-cleaning stainless steel [3] where 5 L of suspension is used, only 150 g of dried TiO_2 powder would be necessary for transport and storage. In this case, the weight gain would be 97%.

Second, if an amount of TiO_2-based sol remains after using it for an application, the product can be dried to be stored for a future use. The cycles of drying-redispersion do not affect the properties of the products and the catalysts can be recycled.

Third, this powder can be very easy to use and can be very flexible for the user. In the form dried under ambient air (containing acid) this powder can be used without any additional chemicals, just by mixing the powder in water. In the form dried at 100°C, the user can select the acid used for the redispersion and adapt the solution to the application.

Fourth, the colloid can be stored for several years and maintains its properties (Tables 2 and 3). This is a very important advantage for a chemical product, to be efficient during use and to be very stable and safe during storage.

Finally, the secondary doping of the redispersed pure TiO_2 (TiO_2+Fe0.5 sample) shows homologous properties to the TiO_2/Fe0.5 sample (Table 1). Moreover, the Fe molar percentage stays constant through the redispersion (Table 1) showing that no doping is lost. So, from pure TiO_2, it is possible to dope with one or several elements [18] to improve or add properties to the desired material. For example, doping with iron increases the photocatalytic activity of the powder (Table 1) by photo-Fenton reactions [18]. An industrial user could adapt the composition of this product during the redispersion steps.

A comparison can be made with the commercial photocatalyst Degussa P25. This material is composed of crystalline TiO_2 (anatase-rutile phases), with S_{BET} value = 60 m^2/g [40]. The photoactivity of P25 is lower than that obtained with the pure TiO_2 (Table 1). To obtain a stable colloid of P25, adding it to water with acid is not enough, a surface functionalization [41] or a multiple step process [42] must be used, increasing the number of steps required to produce a stable P25 sol in order to form films on different substrates.

This synthesis has several other advantages compared to the commercial Degussa P25 catalysts: (i) TiO_2 active powders are obtained at low temperature; (ii) the synthesis method is more eco-friendly (the solvent is water); (iii) the synthesis protocol is easy; (iv) the synthesis protocol is

not expensive because the only cost is the TiO_2 precursor (titanium tetraisopropoxide), while the synthesis of commercial Degussa P25 photocatalyst involves the use of an aerosol process which is known to be expensive, environmentally "unfriendly", and involves high temperature treatments (1000–1300°C) [8].

5. Conclusions

In this work, the property of redispersion of colloids composed of TiO_2 nanocrystallites is studied. Three colloids are considered: one pure and two Fe-doped TiO_2 colloids. Initially, these three colloids are produced by an easy aqueous sol-gel synthesis using precipitation-acidic peptization of Ti precursor to produce an anatase-brookite TiO_2 colloid. Of the two Fe-doped TiO_2, one is doped during synthesis (primary doping) and the other is doped after the synthesis (secondary doping). The three colloids are composed of crystalline TiO_2 particles around 7 nm, present a specific surface area around 200 m^2 g^{-1}, and good photocatalytic properties tested on p-nitrophenol degradation under low energy light.

The powders obtained by air drying of these three colloids are redispersed in water to produce a colloid, which is compared to the initial one. For each colloid, 5 cycles of drying-redispersion are achieved. The results show that similar products are obtained between the cycles, maintaining homologous properties of colloids for the particle size, zeta potential, texture, crystallinity, and the photocatalytic activity.

This property of redispersion is mainly due to the nitric acid used in the synthesis, which decreases the pH of the colloid and protonates the surface of the TiO_2 nanoparticles, leading to a high number of surface charges. The electrostatic repulsions between aggregates allow a

stable sol to form, keeping the same aggregate sizes and zeta potentials through the redispersions. When samples are dried under ambient air, nitric acid stays at the surface and between nanoparticles allowing its redispersion when it is mixed with water. If the powders are dried at 100°C, acid is removed and the redispersion in water is only possible if an acid (HNO_3, HCl, or H_2SO_4) is added.

A stability study of all the produced colloids was made over two years, by following the evolution of the macroscopic aspect and the physico-chemical properties of these sols. This study showed the high stability of the produced colloids. Acid seems to be the main factor for the stability.

The redispersable property can be very useful for industrial applications. In the dried form, it allows the volume and weight to be greatly reduced during transport. Moreover, results show that the pure TiO_2 powder can be doped during its redispersion step allowing an industrial user to adapt the composition of the final product depending on the application. The comparison with commercial Degussa P25 shows that the photoactivity of P25 is lower than the samples synthesized in this work, and its redispersion in acidic water is not possible without prior surface functionalization or multiple step processes.

Compliance with ethical standards

Conflict of interest: The authors declare that they have no conflicts of interest.

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