Dispersion and stability of TiO$_2$ nanoparticles synthesized by laser pyrolysis in aqueous suspensions

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Abstract. Nanoparticles of titanium dioxide (TiO$_2$) were synthesized by the laser pyrolysis method at pilot scale using an organometallic aerosol injected in the reactor. In order to secure the global process of nanoparticle production, we investigate the liquid recovery of the raw powders. The goal was to recover the nanopowders directly in water at the exit of the reaction zone mainly for safety reasons. For that, the dispersion of TiO$_2$ nanopowder in water using a dispersing agent was optimized and comparison of the powder characteristics produced after a dry or a liquid recovery was done.

1. Introduction
In the framework of the European Project NANOSAFE2, the development of secure industrial production systems and safe applications is of major interest. To achieve this goal, we worked on the development of equipment able to collect in liquids the nanoparticles produced by gas-phase processes such as laser pyrolysis [1, 2]. Hence, synthesis and liquid collection of TiO$_2$ nanoparticles was developed on one hand and on the other hand, dispersion in water and stability of TiO$_2$ nanoparticles synthesized by laser pyrolysis was studied.

In the perspective to recover/collection in water the TiO$_2$ nanoparticles produced by laser pyrolysis, studies were held to optimize the dispersion and the stability of the suspensions of TiO$_2$ nanoparticles. Different type of dispersing agents [3-5] may be added to the suspensions to favour the slurrying of the nanoparticles in the liquid and to produce stable suspensions for storage and applications. The influence of different parameters on the dispersion and the stability was studied.

2. Effect of the Specific surface Area (SSA) on the stability
The specific surface area ($S_{BET}$) of as-grown nanopowders was determined by the Brunauer-Emmett-Teller (BET) method using nitrogen adsorption. A first study compared the evolution in time of suspensions for TiO$_2$ nanoparticles with different specific surface areas.

As it is possible to produce nanoparticles having several specific surface areas (SSA) by laser pyrolysis, it appeared interesting to study the stability of the suspensions as a function of the SSA of the powders. Consequently, two powders with different SSA have been selected (06-TiO-14 →
27 m²/g and 06-TiO-20 → 140 m²/g) to study the effect of the SSA on the dispersion and stability behaviour in pure water.

Stability is measured on the basis of Zeta potential measurements. The Zeta potential measurements (by means of the electrophoretic mobility) were performed on a Malvern Nano ZS equipment. A Zeta potential (ζ) of at least 30 mV (positive or negative) is normally required to achieve a reasonably stable dispersion.

The Figure 1 presents the Zeta potential (ζ) for the two powders synthesized by laser pyrolysis compared to the Degussa powder P25 (SSA = 50 m²/g) immediately after sonication. The powder 06-TiO-14 (27 m²/g) has a similar behaviour to that of the Degussa P25 on all the range of pH (almost the same isoelectric point and Zeta potential). The powder 06-TiO-20 (140 m²/g) displays a different behaviour. For this powder, the isoelectric point is clearly shifted toward the low pH values.

This difference could be explained by the differences of the SSA and/or of the residual carbon content. Indeed the chemical analysis revealed that the powder 06-TiO-20 contain 16 wt.% of carbon whereas its colour (between light grey and white) is close to that of 06-TiO-14 which contains only 0.7 wt.% of carbon. This surprising difference of carbon content could explain the results but it has to be confirmed by additional carbon dosages.

The Figure 2 and Figure 3 present the effect of the powder on the stability of the suspensions at a concentration of 0.02 wt %. Each measurement of ζ-potential versus pH was done after magnetic stirring for 20 minutes followed by an ultrasonic treatment of 6 minutes of the suspension. According to the Figure 2, the Degussa P25 appears to be the most stable powder in pure water whatever the pH value up to 790 h. Nevertheless, the Degussa P25 based suspension flocculates very rapidly which should indicate a strong agglomeration of the nanoparticles.
Figure 3 (a) shows an evolution in time of the pH stability range for the powder 06-TiO-14 (27 m²/g). Thus, stability remains unchanged over 910 hours above pH 8.5 whereas a significant decrease of the stability is noted in the low pH range after 100 hours.

For the 06-TiO-20 powder (140 m²/g), Figure 3 (b) shows that the stability remains unchanged over more than 1000 hours in the low pH range (below pH 3). On the other hand, a decrease of the stability range is noted in the high pH range (above pH 6.2 after 144 hours and above pH 7.5 after 1150 hours.

3. Effect of the free carbon content on the stability

We performed a study on the effect of the free carbon content upon the powder characteristics. For that, we apply to a chosen powder a thermal treatment at 460°C, which allows removing completely the free carbon. That way, we were able to compare the characteristics of two powders differing only by their free carbon content. For this comparison, we measured the Zeta potential of aqueous dispersions of different TiO₂ nanoparticles produced by laser pyrolysis, before and after thermal treatment. Result is that around pH = 7 to 8, pH of distilled water used, suspensions with no free carbon content are less stable. This result is confirmed by visual observation of the evolution in time of the suspensions. Same behaviour is observed for suspensions with a dispersing agent (10 different were tested) (Figure 4).
Zeta potential was also investigated as a tool to predict dispersion stability with the same result. For the 4 different powders tested, we find again a lower stability around pH=7.5, after thermal treatment at 460°C, that is after free carbon removing (Figure 5).

Characterization of the particle size distribution was performed by Dynamic Light Scattering (DLS). DLS measures the Brownian motion of the particles and relates it to the particle size. Nanoparticles were mixed with solvent using a sonic probe. Different dispersion mediums were tested (ethanol, acetone and distilled water). The lowest mean size intensity distributions were obtained with the aqueous dispersions. The lowest values measured were around 150 to 200 nm that is much higher than individual particle size (between 12 and 80 nm, as measured by BET). We conclude then that, dispersed in a liquid, the TiO$_2$ nanoparticles form aggregates around 200 nm. This information may be of interest for the toxicity impact and studies. Moreover, as shown on the Figure 6, we find again a lower stability in water, around pH=7.5, for the powders treated at 460°C (particles form larger aggregates).

Microscopic studies have been performed by AFM and TEM to analyze the particle size and shape of the TiO$_2$ nanoparticles revealing for some the presence of free carbon originating from the organic part of incompletely pyrolysed reactant (Figure 7 and Figure 8).
4. Changes in the suspension stability behaviour induced by the addition of dispersing agents

Different dispersing agents were tested for 06-TiO-14, 06-TiO-20 and Degussa P25. The Figure 9 presents the Zeta potential as a function of the dispersant amount (dwb%: dry weight percentage of the TiO$_2$ powder basis) for the powders 06-TiO-14, 06-TiO-20 and Degussa P25. The results show that for 06-TiO-14, Reotan LA [7] and Dolapix® PC 21[8] seem to be the best dispersants. Both of them are synthetic polyelectrolytes (ammonium polyacrylate type). In this case, the deflocculation effect is a result of electrochemical interaction between the functional groups of the additive and the surface of the ceramic particles.

Reotan LA seems also to be one of the best dispersants for 06-TiO-20 and for the Degussa P25. That way, Reotan LA appears to be the more “universal” dispersant agent for the TiO$_2$ nanoparticles tested. The highest values of Zeta potential are obtained for the laser pyrolysis powder compared to the Degussa powder. This is clearly visible on the Figure 10 showing the Zeta potential for all the powders as a function of the amount of dispersant (% of the mass of powder). In the pH range of these measurements (pH of distilled water used between 7 and 8), it is possible to get Zeta potential values between -40 and -55 mV for laser pyrolysis powders whereas the Zeta potential value for the Degussa P25 is only between -20 and -35 mV.
As shown on Figure 11, the addition of a dispersing agent may modify deeply the pH stability range of the suspensions. On the left graph (a), the 06-TiO-14 based suspension is initially stable for pH values below 4 and above 8.5. After the addition of 18 dwb% of Reotan LA, the suspension is stable for pH values above 5.3. On the right graph (b), after the addition of polyethylenimine (PEI) an aqueous suspension of 06-TiO-20 become stable upon the whole range of pH studied (from 2 to 11). This behaviour was observed with different dispersants tested and could be of interest following the application.

**Figure 9.** (a) Effect of the different dispersants tested amount on the ζ-potential of 06-TiO-14 suspensions. (b) Effect of the different dispersants tested amount on the ζ-potential of 06-TiO-20 suspensions. (c) Effect of the different dispersants tested amount on the ζ-potential of P25 Degussa suspensions.

**Figure 10.** Comparison of the effect of Reotan LA amount on the ζ-potential of different TiO\textsubscript{2} nanoparticles suspensions.

**Figure 11.** ζ-potential versus pH (40mg/200mL distilled water).
- a) 06-TiO-14 nanoparticles suspension initially and with the addition of 18 dwb% of Reotan LA.
- b) 06-TiO-20 nanoparticles suspension initially and with the addition of 15 dwb% of PEI.
5. **Comparison of the powder characteristics produced after a dry or a liquid recovery**

Comparison of the powder characteristics produced after a dry or a liquid recovery was performed. Specific surface areas and density are almost the same and the main difference concerns the carbon content which is much higher after a dry recovery. As the TTIP (titanium isopropoxide), reactant used for the TiO$_2$ synthesis, is very reactive with water, non pyrolysed part of it may hydrolyse during liquid collection and leads to different volatile sub-products which disappear during powder recovery. At last, the characteristics reproducibility for the powders issued from the liquid recovery means was tested. A good reproducibility was noticed for specific surface area, density and anatase versus rutile rate (Table 1).

| Ref.   | Liquid: | Carrier gas flow rate Ar (l/min) | Incident laser power (W) | $S_{BET}$ (m$^2$/g) | Density (g/cm$^3$) | Anatase (wt%) | Rutile (wt%) |
|--------|---------|---------------------------------|--------------------------|----------------------|-------------------|--------------|-------------|
| 07-TiO-02 | W + D   | 60                             | 4550                     | 54                   | 3.4               | 93           | 7           |
| 07-TiO-03 | W(80%) + E(20%) + D | 55                             | 4550                     | 47                   | 3.4               | 98           | 4           |
| 07-TiO-04 | W(80%) + E(20%)   | 60                             | 4550                     | 46                   | 3.4               | 97           | 3           |

**Table 1.** Characteristics of the powders after drying for different solvents used for liquid recovery.

6. **Conclusion**

Conditions have been optimized to produce stable TiO$_2$ nanoparticle aqueous suspensions. We determined the best dispersing agent and its best dry weight percentage of the TiO$_2$ basis to be added in order to obtain well dispersed suspensions and the most stable in time. Moreover, we show that liquid recovery of the nanopowders directly at the exit of the pilot reactor is possible and that powder characteristics after a liquid recovery are the same as after a dry recovery.

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