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Colloidal stability of nanosized titania aqueous suspensions

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Abstract

In this work the colloidal behaviour of three different TiO_2 nanopowders in water is studied. A commercial powder of anatase and another of rutile were used for this study. For comparison purposes, a cryogel of anatase synthesised by a particulate sol–gel route and freeze-dried was also studied. All three powders were characterised by scanning electron microscopy, specific surface area measurements and X-ray diffraction. Diluted aqueous suspensions were prepared and characterised in terms of particle size distribution and zeta potential, using dynamic light scattering and laser Doppler velocimetry principles, respectively. All suspensions were prepared using an ultrasounds probe for mixing times ranging from 0 to 5 min. Colloidal stability was studied as a function of pH, type and concentration of dispersants (polyacrylic-based deflocculant and citric acid) and mixing time. Stable suspensions of commercial nanosized powders were obtained with polyelectrolyte contents of 1.0–1.5 wt.%. No stable suspensions of the cryogel were obtained with polyelectrolyte, requiring in this case the use of citric acid as deflocculant. It was observed that neither the size distribution nor the zeta potential values were affected by the sonication time.

Keywords: TiO_2; Nanopowders; Colloidal behaviour; Zeta potential

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1. Introduction

The study of nanomaterials has reached great importance in the last years, because of their huge potential applications in many fields of science. A fundamental aspect to be considered is the complexity of working with nanopowders, because of their toxicity and their strong tendency to spontaneously agglomerate due to their large surface area and surface properties.[1] For this reason, the manipulation of nanopowders in wet conditions is preferred and has demonstrated to allow obtaining higher uniformity.[2] At this level, the surface forces play a fundamental role on the stability of suspensions,[3–7] as flocculation may occur spontaneously through London-van der Waals attractive forces. The tendency to coagulate can be overcome by means of electrostatic repulsions between similarly charged particles, repulsive non-DLVO forces arising from solvation of adsorbed layers, or most frequently, by an electrosteric mechanism with the use of polyelectrolytes.

Titania-based materials have attracted great attention due to their photovoltaic and catalytic activity, among other applications in different fields such as clean energy production (solar cells), self-cleaning surfaces, water treatments, etc.[8,9] For such requirements nanosized powders are used as coatings on adequate substrates. The coating processes and treatments must be integrated, as much as possible, into the actual ceramic process/practice, so contributing to exploit the high expertise level presently achieved by the ceramic industry and to make competitive the production costs. Hence, when colloidal suspensions are used to produce such coatings an in-depth study of the surface and colloidal behaviour of those powders is needed as well.

The dispersing conditions of TiO_2 particles in either aqueous or non-aqueous media have been studied elsewhere using any of the above mentioned mechanisms of dispersion.[10–14] Although the dispersion of nanosized titania powders has received some attention in the last years it is not yet enough and more work is necessary.[15,16]

The aim of this work was to study the colloidal behaviour of nanosized titania powders in aqueous medium in terms of

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particle size distribution and ζ-potential, evaluating the effect of dispersants nature and concentration and the effect of mixing time using an ultrasounds probe. Two commercial nano-powders were selected taking into account the different crystalline phases of titanium dioxide, rutile and anatase. The synthesis of a third powder with much larger surface area prepared through a sol–gel route was studied for comparison purposes.

2. Experimental

2.1. Characterisation of starting nanopowders

Three different TiO_2 nanopowders were employed in this study: a commercial anatase (Inframat® Advanced Materials™, USA), which is supplied as a sprayed powder to facilitate handling, a commercial rutile (Tayca Corporation, Japan), and an anatase titania cryogel synthesised in the laboratory. The synthesis was done by a sol–gel route in which $Ti(OPr^i)_4$ was hydrolysed into a flask containing a stirring mixture of H_2O and HNO_3 at pH 1. The final water-to-alkoxide molar ratio was 30:1. The mixture was stirred for 3 days at 30 °C and then freeze-dried, obtaining a high surface area cryogel.

The three starting materials were characterised by field emission gun scanning electron microscopy, FEG-SEM (Hitachi S-4700 type I, Japan). The control of the crystalline phases was made by X-ray diffraction (D5000, Siemens, Germany). Specific surface area was determined using the single point BET method (Monosorb Surface Area Analyser, MS-13, Quantachrome, USA). The average particle size values (d_{BET}) were calculated from specific surface area measurements, assuming spherical, homogeneous primary particles, through the following equation

$$d_{\mathrm{BET}} = \frac{6}{S_{\mathrm{BET}}}\rho \qquad (1)$$

where S_{BET} is the measured specific surface and ρ is the material density. The obtained values are reported in Table 1. The titanium oxide synthesised via sol–gel in the laboratory has the highest value, even though it is composed by small flakes rather than particles.

2.2. Characterisation of nanopowder suspensions

After characterising the dry powders, the colloidal behaviour of powders in water was studied. The stability against pH was studied by zeta-potential measurements in order to determine the isoelectric point (IEP). For these measurements, dispersions of TiO_2 powders were prepared to a concentration of 0.1 g/l using KCl solution (10^{-2} M), as inert electrolyte. The pH was measured with a pH-meter (Titrino DMS 716, Metrohm, Switzerland), and was adjusted by using KOH and HCl solutions. In this first stage of the study, the suspensions were aged for 24 h at room temperature, using an orbital shaker. All suspensions were prepared using an ultrasounds probe (UP 400S dr.hielscher GmbH, Germany) for homogenisation.

Table 1
Specific surface of the three nano-powders

Sample	S_{BET} (m^2/g)	d_{BET} (nm)
Anatase	46 ± 3	34
Rutile	28 ± 2	55
Cryogel	142 ± 7	11

Zeta potentials (ζ) were measured by laser Doppler velocimetry (Zetasizer NanoZS, Malvern, UK), applying the Henry equation:

$$U_{\mathrm{E}} = \frac{2\varepsilon\zeta f(ka)}{3\eta} \qquad (2)$$

where ζ is the zeta potential, U_E the electrophoretic mobility, ε the dielectric constant of water, η the medium viscosity and $f(ka)$ is the Henry's function. Calculations of the mobility were done considering the Smoluchowski approximation ($f(ka) = 1.5$).

The dilute aqueous suspensions were also studied in terms of particle size distribution using the dynamic light scattering principle, available in the same instrument used for zeta potential determinations (Zetasizer NanoZS, Malvern, UK). The particle size was measured to evaluate any break-down of the agglomerates.

Suspensions were also prepared using deflocculants. A commercial salt of polyacrylic acid-based polyelectrolyte, DURAMAX™ D-3005 (Rohm & Haas, USA) was used although some tests were performed also with Citric Acid (PROBUS, Spain) for comparison purposes. Deflocculant concentrations of 0.2%, 0.5%, 1.0%, 1.5%, and 2.0 wt.% (with respect to the TiO_2 total mass) were studied. At this stage of the work, all suspensions were prepared with the aid of 1 min, sonication to deagglomerate the nanopowder, followed by 2 min sonication after the dispersant addition, and maintained in agitation using an orbital shaker for 30 min, to allow the complete adsorption of deflocculant on the nanopowder surface. Once the dispersant concentration was optimised, the effect of sonication time was studied by applying sonication times, 0, 1, 2, 3 and 5 min, US.

3. Results and discussion

3.1. Characterisation of starting nanopowders

X-ray diffraction (XRD) patterns of the three considered materials are shown in Fig. 1. It can be noted that the XRD patterns of the two commercial powders are highly crystalline. The XRD pattern of the synthesised cryogel presents the anatase peaks, but the signal is less intense, and the peaks are less defined, indicating lower crystallinity and/or a lower crystallite size.

Microstructural observations made by FEG-SEM for the commercial anatase-TiO_2, (Fig. 2) show that the particles are agglomerated forming spherical granules of several dimensions, with the typical morphology of spray dried powders. At higher magnifications, primary particles of spherical shape and dimensions of approximately 40 nm can be distinguished.

Microstructural observations made for the commercial rutile sample (Fig. 3) show that it is constituted by agglomerates of rather heterogeneous dimensions. At higher magnifications,

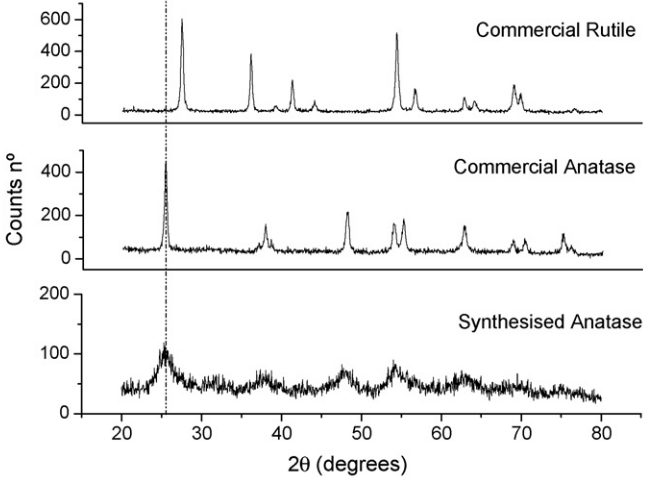

Fig. 1. XRD patterns of the three nano-powders.

nanometric particles with spherical shape and dimensions of 40–50 nm in diameter can be distinguished. The surface area is significantly lower than that of the commercial anatase (Table 1).

Similarly, Fig. 4 shows the microstructure of the powder synthesised by sol–gel followed by freeze-drying. As mentioned above it is not a real powder but a cryogel, which is constituted by nanometric particles that build up submicronic particles and platelets of rather great dimensions (up to 100 μm) and sharp edges. This fact explains the higher S_{BET} values of the anatase cryogel.

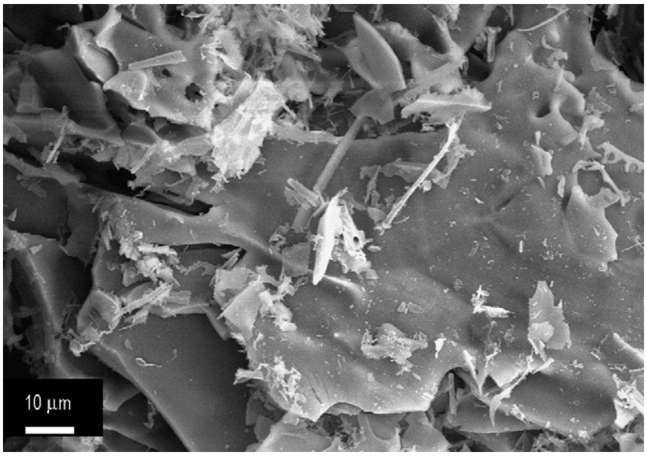

Fig. 4. FEG-SEM images at different magnification of anatase xerogel.

3.2. Characterisation of nanopowder suspensions

In Fig. 5 the zeta potential values measured for the two powders and the cryogel as a function of pH are plotted. In the case of commercial anatase, the measured IEP occurs at about 5.3. For commercial rutile, it is observed that until pH values around 5 the zeta potential is about +35 mV, but at pH values between 6 and 7 there is a rapid decrease of the zeta potential, the IEP occurring at pH 6.3. The two commercial powders give a pH 6 when immersed in water, very near the isoelectric points and thus leading to unstable suspensions. Finally, the anatase-TiO_2 synthesised by sol–gel behaves as the commercial anatase,

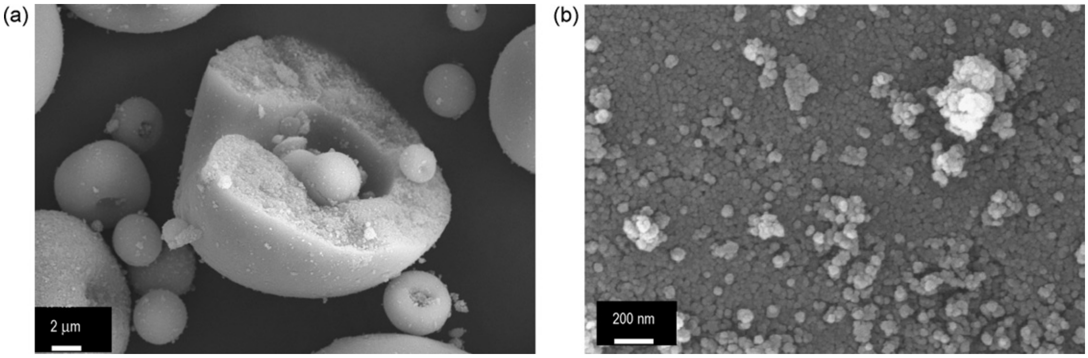

Fig. 2. (a) and (b) FEG-SEM images at different magnification of commercial anatase nanopowders.

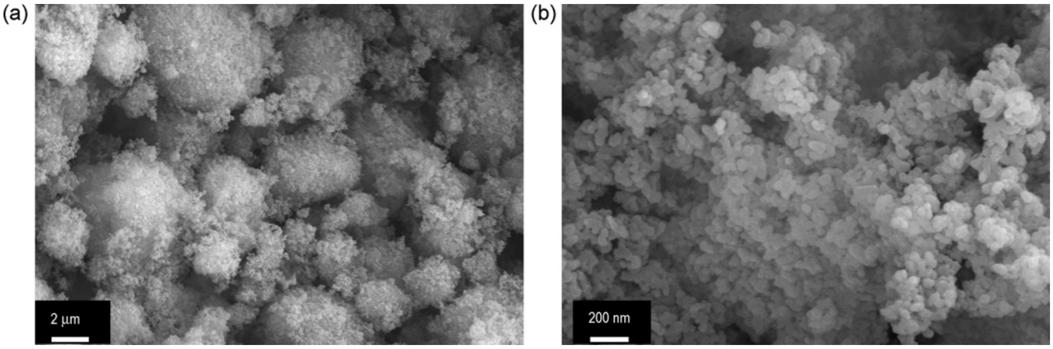

Fig. 3. (a) and (b) FEG-SEM images at different magnification of commercial rutile nanopowders.

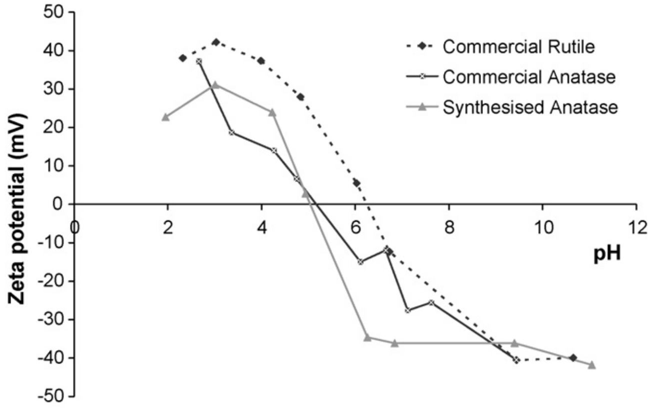

Fig. 5. Zeta potential vs. pH of the three powders.

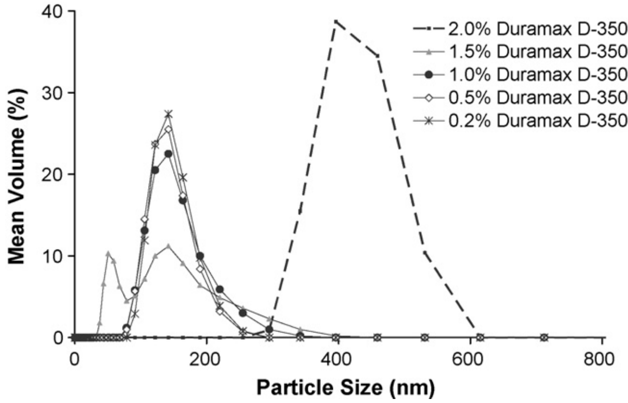

Fig. 6. Size distribution of commercial anatase at different polyelectrolye concentrations.

showing a similar zeta potential curve, the IEP occurring also at 5.0. The starting pH when immersed in water was 4.3, thus presenting positive surface charge. Kosmulski[17] made an extensive review of the points of zero charge of TiO_2, showing that it could change from 2.0 to 8.9, although more than 70% of the papers reporting the isoelectric point or the zero point of charge fall in the range of pH 5–7. This author concluded that the PZC of titania is rather insensitive to the crystallographic structure (anatase versus rutile) or to the choice of experimental method and established a 'recommended' value of pH 5.9 for both polymorphs.

For a better understanding of the colloidal behaviour of the studied powders, the particle sizes of the different suspensions were determined in order to evaluate the formation/destruction of agglomerates. To do so, a previous analysis of the adequate concentration of particles of the suspension has to be done to take a reliable measurement in the dynamic light scattering instrument used in this work. Several dispersions were prepared and tested at different concentrations, with the aim to find the better measuring conditions, in terms of instruments reliability, through the particle size distributions and it was experimentally observed that the better dispersion of the particles was reached at the following concentrations: 0.01 wt.% for both the commercial and the synthesised anatase-TiO_2, and 0.001 wt.% for commercial rutile.

During the preparation of the sample it was noticed that the commercial anatase nanopowder did not sediment, and the suspension was opaque even for very dilute systems. However, the dispersion became more opaque with time, as particles agglomerate. Without dispersant the measured average diameter was about 120 nm, thus demonstrating that particles are agglomerated forming clusters of a few units. In the case of rutile, the sedimentation of the powder is directly detected by visual inspection, although the measured average diameter was also about 120 nm. For the synthesised anatase cryogel, the sizes are higher than for the commercial powders, as can be seen in the SEM pictures. Commercial powders have a mean size of around 120 nm whereas the synthesised powder has around 400 nm.

To improve the dispersion state, the suspensions were stabilised using a polyelectrolyte. Fig. 6 shows the size distribution measured for the commercial anatase-TiO_2 with different concentrations of dispersant added. The plot is similar for concentrations up to 1.0 wt.%, the mean diameter being around 120 nm (agglomerates), which is the same value obtained without dispersant, but at a concentration of 1.5 wt.%, a bimodal curve is recorded, thus suggesting that agglomerates are breaking down. The excess of deflocculant (2.0 wt.%) leads to some reagglomeration, probably due to polymeric bridging of free polyelectrolyte, and particle size increases.

In the case of rutile–TiO_2, deflocculant additions have a negligible effect on particle size distribution (Fig. 7), which gives a non-Gaussian curve with an extended tail towards larger sizes and an average value of 120 nm in all cases.

The stability of the suspensions as a function of polyelectrolyte concentration was studied in more detail with measurements of zeta potential (Fig. 8). In this phase of the study the nanopowders were firstly dispersed in water using 1 min sonication, until the soft agglomerates were partially broken. Later, the dispersant was added and the slurries were further sonicated for 2 min, to promote the adsorption of the deflocculant onto the powder surface. In the case of anatase, a maximum zeta potential of −58 mV was obtained for 1.5 wt.% polyelectrolyte, whereas a maximum zeta potential of −42 mV was obtained for rutile adding 1.0 wt.% polyelectrolyte. It was observed that the pH slightly increased from 5.8 to 6.3 as the deflocculant content increased from 0.2 to 2.0 wt.%, for both commercial powders.

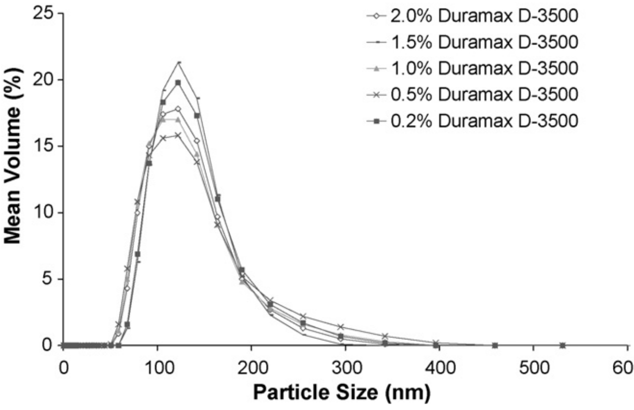

Fig. 7. Size distribution of commercial rutile at different polyelectrolye concentrations.

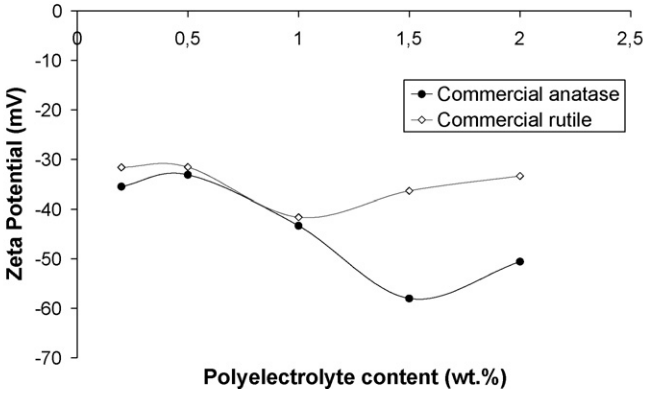

Fig. 8. Zeta potential vs. polyelectrolyte concentration for commercial anatase and rutile.

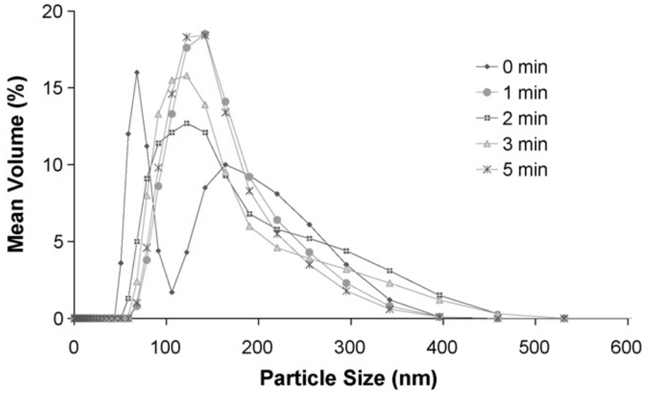

Fig. 10. Size distribution of commercial anatase with citric acid at different US time.

Measurements without deflocculant were shown in Fig. 5, and are not included in this one because the pH changes.

To further optimise the dispersion of the commercial powders the effect of US mixing time on the zeta potential was studied for suspensions prepared to a solids concentration of 0.01 wt.% and optimised polyelectrolyte content (1.5 and 1.0 wt.% for anatase and rutile, respectively). It was observed that neither the size distribution nor the zeta potential values were affected by the sonication for mixing times up to 5 min, and the pH values maintained always within the range 5.9–6.1. Despite the high zeta potential absolute values, the size distribution measurements show that the particles have a cluster-like behaviour, and what is measured is the mobility of such clusters.

Suspensions of synthesised TiO_2 cryogel with concentration of 0.01 wt.% were also studied but although the experiments were repeated up to three times it was not possible to take representative results. This seems to indicate that polyelectrolytes are not adequate dispersing agents for this agglomerated cryogel, since the adsorption of medium to large sized chain molecules of polyelectrolyte becomes much more difficult than in the case of single, dispersed particles.

The same procedure described so far was followed using citric acid as dispersing agent. Citric acid is a short chain molecule but has three carboxylic groups that can lose a proton in solution, generating citrate ions.[18] These ions help to control the pH of acidic solutions. When citric acid is added to an aqueous suspension, it dissolves immediately. In the case of commercial anatase, the citric acid added in various concentrations had no significant effect on size distribution: the mean particle size measured is always in the range 120–150 nm. However, it had a noticeable effect on the zeta potential (Fig. 9). A minimum of −43 mV is obtained for 0.5 wt.% of citric acid, which is larger than the absolute value obtained for pH 6 without deflocculant (−12 mV) but lower than the one obtained with optimised polyelectrolyte content (−58 mV). The pH values measured for suspensions of commercial anatase prepared with citric acid do not change significantly. pH slightly decreases from 5.8 to 5.2 as the citric acid content increases from 0.2 to 2.0 wt.%. In the case of rutile, the greatest dispersion stability was obtained for a citric acid concentration of 1.5 wt.%, where the zeta potential had a value of −29 mV (Fig. 9). However, size distributions do not vary with the different citric acid concentrations, thus meaning that citric acid is not able to disperse the agglomerates and was not used for further studies. In the case of synthesised titania, the zeta potential values go from the positive values obtained for the powder without dispersant to negative values as the concentration of citric acid added increases.

For the optimised concentrations of citric acid, the influence of US mixing time on particle size and zeta potentials was also studied. It was observed that for low US times (2–3 min) there

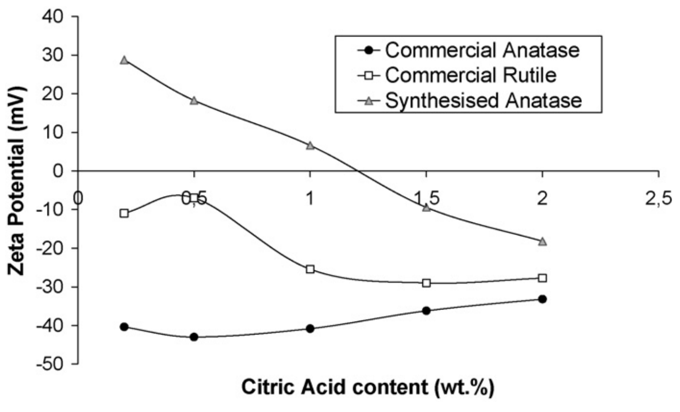

Fig. 9. Zeta potential vs. citric acid concentration for the three powders.

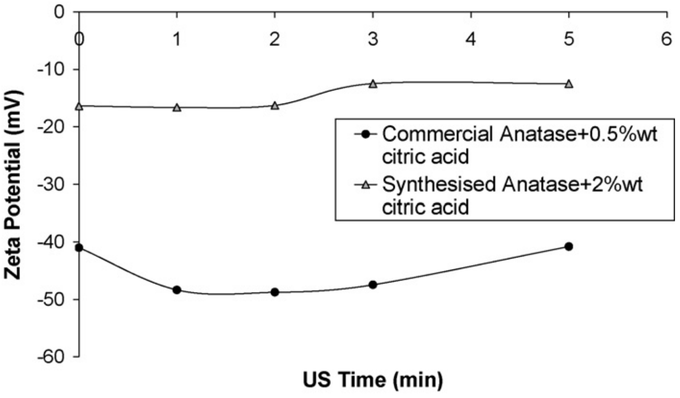

Fig. 11. Zeta potential vs. US mixing time for commercial and synthesized anatase with optimized citric acid concentration.

is a bimodal size distribution (Fig. 10), whereas for longer mixing times the curves are monomodal and give an average size of around 120 nm, that is, deagglomeration takes place. The measurements of zeta potential with citric acid reveal a slight variation with a maximum zeta potential (−49 mV) after 2 min US, as observed in Fig. 11 for both anatase samples (commercial powder and cryogel). It was observed again that sonication had no influence on the suspension pH.

4. Conclusions

The colloidal behaviour of commercial nanosized powders of rutile and anatase in water has been studied, as well as that of a cryogel obtained by a sol–gel route. The isoelectric point of these powders occurs at pH values ranging from 5.0 to 6.3, in good agreement with the values typically reported in the literature. Microstructural observations demonstrate that commercial powders are formed by soft agglomerates of small particles with ∼40 nm in diameter, whereas the cryogel is formed by flakes of a few hundreds of nanometers. The particle size measured by dynamic light scattering strongly depends on the measuring conditions, the lower diameter being around 120 nm, that is, small groups of several particles.

Large zeta potentials are obtained for commercial nanopowders dispersed with a polyelectrolyte, but it is not possible to obtain well-dispersed suspensions of the cryogel with polyelectrolytes. For the cryogel, citric acid has demonstrated to be more efficient dispersant. In every case the sonication time has no influence on particle sizes and zeta potentials, e.g. on the stability of dilute suspensions.

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