Chem. Mater. **2008,** *20,* 4161–4165

Determination of Peptization Time of Particulate Sols Using Optical Techniques: Titania As a Case Study

M. T. Colomer,* J. Guzmán, and R. Moreno

Instituto de Cerámica y Vidrio, CSIC, c/Kelsen, 5, Cantoblanco 28049, Madrid, Spain

Received December 13, 2007. Revised Manuscript Received February 27, 2008

Colloidal sol−gel technology is widely used as a powerful synthesis route. It consists of two main stages, hydrolysis and peptization. The quantification of peptization time is necessary to improve the processing control and enhance product reliability. However, the peptization time is normally estimated by simple visual inspection. The aim of this work is to establish for the first time a procedure to quantify the peptization time. For such purposes, different optical techniques have been used, in particular the measurements of particle size distribution by laser diffraction and by dynamic light scattering. The experimental mismatch between both series of data allows determining the peptization time, and the results are in good agreement with turbidimetry measurements through the transmission of near-infrared light source. The synthesis of titania has been selected as a case study because anatase presents a large interest in many different applications. It has been demonstrated that peptization time significantly increases as the synthesis temperature decreases: Sols prepared at 25 °C present a peptization time of ~95 h, sols prepared at 30 °C need ~72 h for a complete peptization, sols synthesized at 35 °C present a peptization time of ~45 h, and those prepared at 50 °C show a peptization time of ~9 h. The peptization time for sols prepared above 80 °C is quite short; the synthesis is less reproducible and the risk of uncontrolled gelation increases. The average particle size changes from ~13 nm for sols prepared at 25 °C, 20 nm for sols prepared at 35 °C and, to ~30 nm for sols prepared at 50 °C. The resulting xerogel has been characterized in order to demonstrate the suitability of the synthesis procedure.

Introduction

There are two basic methods for attaining stable sols. The first one is based on the controlled hydrolysis and polycondensation of metal alkoxides or other organo-metallic compounds in nonaqueous solvents.[1–4] The second common method for a sol synthesis is based on the preparation of stable colloidal suspensions, which can be obtained by complete hydrolysis of metal salts or alkoxides.[5,6] Hydrolysis yields precipitates of hydrous oxides, which can then be peptized with an acid or a base. Sols prepared by the latter method present usually a much longer stability time. Peptization takes place as a result of the repulsion between electric double layers around colloidal particles, developed during charging of particles surface. Peptization involves three possible processes that could occur simultaneously: (1) agglomerates break down into particles of colloidal dimensions by providing chemical, thermal or mechanical energies; (2) particle charging by proton adsorption, which in turn stabilizes the suspension through electrostatic repulsion; (3) particle reagglomeration may occur as a consequence of incomplete peptization. The overall process of peptization is complex and the average particle size in the final product will depend on the relative rates of break down and aggregation. In this process, a number of factors must be considered: (1) suspension pH, which determines the surface potential of particles; (2) ionic strength that controls the thickness of the double layer surrounding the particles; (3) temperature, which not only provides energy for breaking the precipitates but also causes an increase of the collision rate leading to particles reagglomeration[5] (see references therein). In summary, the peptization process modifies the particle surfaces and leads to a reduction of the agglomerate size.

In practice, complete and instantaneous hydrolysis of a precursor (Titanium alkoxides, $TiCl_4$, TiF_4, ...) takes place for high H_2O/alkoxide ratios, obtaining a white precipitate that undergoes peptization. During the peptization step, the suspension is maintained at a constant temperature for a certain period of time and stable particulate sols with average particle sizes of few nanometers are produced. Unfortunately, based on optical techniques, a fast and simple scientific criterion capable to quantify the peptization time is not yet available. The most common criterion is simply based on the visual appearance of the sol; it is normally considered that peptization has occurred when the sol becomes transparent. Venz et al.[7] reported the use of FT-Raman spectroscopy to study the structures of the titania hydrous oxide precipitates, or hydrolyzed species, produced from pure and

---

* Corresponding author. E-mail: tcolomer@icv.csic.es.

(1) Livage, J.; Henry, M.; Sanchez, C. *Prog. Solid State Chem.* **1988**, *18*, 259.
(2) Dislich, H. *J. Non- Cryst. Solids* **1986**, *80* (1−3), 115.
(3) Zaharescu, M.; Crisan, M.; Simionescu, L.; Crisan, D.; Gartner, M. *J. Sol−Gel Sci. Technol.* **1997**, *8* (1), 249.
(4) Zhang, H.; Finnegan, M.; Banfield, J. F. *Nano Lett.* **2001**, *1* (2), 81.
(5) Bischoff, B. L.; Anderson, M. A. *Chem. Mater.* **1995**, *7* (10), 1772.
(6) Mohammadi, M. R.; Fray, D. J.; Mohammadi, A. *Microporous Mesoporous Mater.* **2007**, 016/j.micromeso.2007.10.015.
(7) Venz, P. A.; Frost, R. L.; Barlett, J. R.; Woolfrey, J. L. *Spectrochim. Acta, Part A* **1997**, *53*, 969.

10.1021/cm703560x CCC: $40.75

modified alkoxides and estimated the time required for no further spectral changes in the system.

Titania sols ($TiO_2 \cdot xH_2O$) have been chosen because titanium oxide is a semiconducting oxide with interesting photoactivity, having applications in different fields such as clean energy production,[8] air and wastewater treatment by degrading different types of pollutants,[9–14] and even photo-killing of tumoral cells.[13] There are three crystallographic phases of TiO_2: anatase, rutile and brookite, the first having higher catalytic activity because of its slightly higher Fermi Level and to its much more hydroxylated surface, as well as the higher recombination velocity of photoinduced electron−hole pairs in rutile.[11,17,18] Nanosized crystal grains of anatase have larger band gap size and higher conduction band level to accomplish, for instance, the reduction of H_2O to H_2, whereas the conduction band level is unfavorably lower in both rutile and larger-grained anatase forms. By comparison, amorphous TiO_2 has a band gap equal to or greater than nanocrystalline anatase, and therefore may have a conduction band level suitable for the efficient photocatalytic reduction of H_2O. However, nearly all photocatalytic studies on TiO_2 have focused on its crystalline forms, as it is commonly accepted that amorphous metal oxides contain high concentrations of defects that will invariably function as rapid electron−hole recombination centers to render them inactive.[18,19] However, hydrated forms of metal oxides often exhibit markedly higher activities.[20,21] For these reasons, in this study, the nanosized anatase phase has been chosen as the desired phase.

In this work, titania sols with a water to alkoxide molar ratio as large as 100:1 have been prepared and studied. Strongly acidic pH (pH 1) was used because the obtained particle size decreases with the synthesis pH[5] and taking into account the total Ti the formed $Ti(OH)_4$ will evolve to $TiO_2 \cdot xH_2O$, as reported elsewhere.[22] The main objective of this work is to control the evolution of the peptization process during the particulate sol−gel synthesis by means of the combination of different optical techniques such as laser diffraction, dynamic light scattering (DLS), and turbidimetry by multiple light scattering. The quantification of peptization time is necessary to improve the processing control and to enhance product reliability.

Experimental Section

Sol Preparation. The alkoxide hydrolysis was carried out by adding titanium(IV) isopropoxide, 97% (Sigma-Aldrich, Germany) to a stirring mixture of deionized water and nitric acid (Merck, Germany) at temperatures of 25, 30, 35, 50, 60, and 80 °C that were kept constant during the whole synthesis process. The prepared sols had a concentration of TiO_2 of 37 g/L, with a 1:100 alkoxide: water molar ratio and a 1:5 H^+:Ti ratio, using HNO_3 as a catalyst (pH 1).

Sol Characterization. The white precipitate obtained from the alkoxide hydrolysis was stirred at a constant temperature (peptization). At the earlier stages of the process, particle size distribution of the suspension was measured by laser diffraction (Mastersizer S, Malvern, U.K.), until the particle size was so small that could not be determined by this technique. Samples of the sols were measured also by dynamic light scattering (Zetasizer Nano ZS, Malvern S, U.K.), throughout the whole synthesis process and once the process had ended to study their aging.

UV−vis spectra were obtained with a spectrophotometer (Perkin-Elmer, USA) at different points of the synthesis process, performing a wavelength scan from 200 to 800 nm.

Considering that laser diffraction (LD) and dynamic light scattering (DLS) give complementary information for different ranges of particle sizes, near-infrared (NIR) light transmission measurements were also performed, as this technique allows continuous measurements even when the reaction is in progress. These measurements were performed by the multiple light scattering principle using a Turbiscan MA 2000 apparatus (Formulaction, France). This equipment has a detection head that moves along the measurement cell acquiring data of the transmitted and backscattered NIR light ($\lambda = 850$ nm) profiles and thus giving important information about the stability of suspensions, especially by looking at the bottom of the cell—where sedimentation takes place—and at the top of the suspension—where other phenomena such as creaming may occur. In this work, the cells were filled to a height of approximately 40 mm but only the first performed measurement of transmitted light, collected at a height of 20 mm from the bottom of the cell—far enough from the bottom of the cell and the top of the suspension—are presented. The rheological behavior and aging of the prepared sols was studied using a rheometer (RS50, Haake, Germany) with a double-cone/plate sensor configuration (DC60/2°, Haake, Germany). Viscosity curves were obtained with a three-stage measuring program with a linear increase of shear rate from 0 to 1000 s^{-1} in 300 s, a plateau at 1000 s^{-1} for 60 s, and a further decrease to zero shear rate in 300 s.

Xerogel Characterization. After validating the peptization criterion, the xerogel obtained from the sol synthesized at 30 °C was dried at room temperature and subjected to thermal treatments at temperatures between 300 and 600 °C, with a dwell time of 1 h and a heating rate of 5 °C/min. The samples were slowly cooled inside the furnace. Crystalline phases were identified by X-ray diffraction, XRD (D5000, Siemens, Germany). The microstructure was studied by means of transmission electron microscopy, TEM (JEOL JEM 4000EX, Japan). Specific surface area measurements were performed by the one point BET Method (Monosorb surface area analyzer, MS-13, Quantachrome Corporation, U.S.A.).

Results and Discussion

Defining the Peptization Criterion. As reported by Bishoff and Anderson,[5] as the peptization time increases the

---

(8) Colomer, M. T. *Adv. Mater.* **2006**, *18* (3), 371.
(9) Ohtani, B.; Zhang, S.; Handa, J.; Kajiwara, H.; Nishimoto, S.; Kagiya, T. *J. Photochem. Photobiol. A: Chem.* **1992**, *2*, 223.
(10) Sclafani, A.; Herrmann, J. M. *J. Phys. Chem.* **1996**, *100* (32), 13655.
(11) Modestov, A. D.; Lev, O. *J. Photochem. Photobiol. A: Chem.* **1998**, *112* (2−3), 261.
(12) Botta, S. G.; Rodriguez, D. J.; Leyva, A. G.; Litter, M. I. *Catal. Today* **2002**, *76* (2−4), 247.
(13) Muneer, M.; Das, S.; Manilal, V. B.; Haridas, A. *J. Photochem. Photobiol. A: Chem.* **1992**, *63* (1), 107.
(14) Pichat, P.; Disdier, J.; Hoang-Van, C.; Mas, D.; Goutailler, G.; Gaysse, C. *Catal. Today* **2000**, *63* (2−4), 363.
(15) Cai, R.; Hashimoto, K.; Itoh, K.; Kubota, Y.; Fujishima, A. *Bull. Chem. Soc. Jpn.* **1991**, *64* (4), 1268.
(16) Bickley, R. I.; González-Carreño, T.; Lees, J. S.; Palmisano, L.; Tilley, R. J. D. *J. Solid State Chem.* **1991**, *921*, 178.
(17) Sun, J.; Gao, L.; Zhang, Q. *J. Am. Ceram. Soc.* **2003**, *86* (10), 1677.
(18) Tanaka, K.; Capule, M. F. V.; Hisanaga, T. *Chem. Phys. Lett.* **1991**, *187*, 73.
(19) Jensen, H.; Joensen, K. D.; Jorgensen, J.-E.; Pedersen, J. S.; Sogaard, E. G. *J. Nanopart. Res.* **2004**, *6*, 519.
(20) Kudo, A.; Tanaka, A.; Domen, K.; Maruya, K.; Aika, K.; Ohnishi, T. *J. Catal.* **1988**, *111*, 67.
(21) Takata, T.; Shinohara, K.; Tanaka, A.; Hara, M.; Kondo, J. N.; Domen, K. *J. Photochem. Photobiol.* **1997**, *106*, 45.
(22) Xu, Q.; Anderson, M. A. *J. Mater. Res.* **1991**, *6*, 1073.

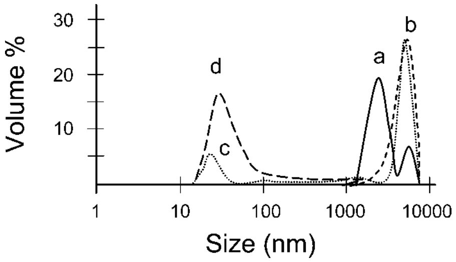

Figure 1. Average size distribution obtained by DLS of agglomerated sols synthesised at 50 °C after reaction times of (a) 0.5, (b) 9, (c) 11, and (d) 18 h.

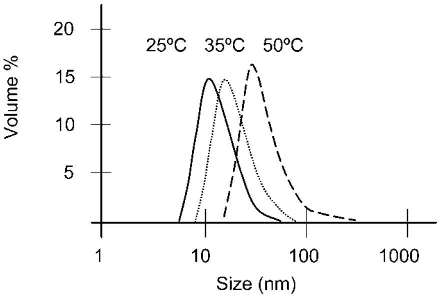

Figure 2. Average size distribution obtained by DLS of sols synthesised at (a) 25, (b) 35, and (c) 50 °C after peptization. pt means peptization time. Peptization time at 25 °C was ~97 h, at 35 °C was ~40 h, and at 50 °C was ~9 h.

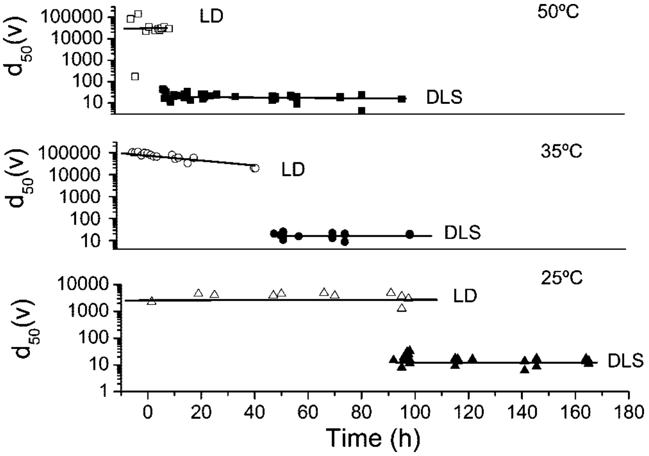

Figure 3. Average particle diameters d_{50}(v) vs peptization time measured for the sols synthesised at temperatures 25, 35, and 50 °C, using laser diffraction (large values at the left of the marked line) and dynamic light scattering (values at the right).

size of the particle agglomerates also increases. However, these authors used only XRD on the synthesized xerogels, but this is not a direct measurement of the sol evolution. In this study, the peptization has been considered unequivocally complete when the agglomerate size reaches a minimum value that is maintained constant with time. In our case, a white $TiO_2 \cdot xH_2O$ (anatase) precipitate is formed that after being stirred for a few seconds yields an unstable, opaque suspension. Afterward, the agglomerates in suspension are broken down into smaller units as mentioned above, and the suspension acquires a translucent whitish aspect that evolves to a transparent sol.

In Figure 1, DLS measurements at different stages of the process are displayed for sols synthesized at 50 °C. Figure 1.a shows that, right after hydrolysis of the alkoxide, a monomodal distribution is obtained with large particle agglomerate size values, close to the detection limit of the instrument (average diameter, d_{50}(v) being 4 μm). Large amounts of precipitates are settling during the measurements and probably the instrument is only capable to detect the finer fraction of particles. Distributions b and c in Figure 1 show that, after several hours, the situation is similar with large amounts of white powder settling at the bottom of the measurement cell. The agglomerate size distribution and the measured d_{50}(v) values significantly decrease to the nanometre scale, where the suspension becomes transparent and no sedimentation occurs (Figure 1d). Similar evolution was found for sols prepared at any other temperature, although the reached size and the time of the reaction changes every time. Figure 2 compares the size distribution measured for the peptized sols synthesized at different temperatures. It can be clearly seen that a single peak is obtained in all cases in which the average particle size changes from ~13 nm for sols prepared at 25 °C, to ~20 nm for sols prepared at 35 °C, and to ~30 nm for sols prepared at 50 °C. These measurements were performed using sols prepared with enough time to ensure that peptization was complete. The combination of these values with those obtained by DLS allows us to estimate the peptization time, as described below.

In Figure 3, the evolution of d_{50}(v) values vs reaction times measured at three different reaction temperatures using both LD and DLS techniques are plotted. Particle sizes were measured at every temperature using both LD and DLS techniques for times ranging between 0 and 150 h. However, LD measurements gave only some signal up to a time *t* and no signal was obtained for longer times. Contrarily, DLS gave reliable data only for times above t, where the measured size is lower. This means that in all cases particle size drops steeply after a certain time that depends on the synthesis temperature, d_{50}(v) evolving from more than several micrometers (large TiO_2 agglomerates, which can be only measured with laser diffraction) to values of 10−20 nm primary particles or small groups of several units, and can be only measured by DLS. Because LD provides information on a size range different to the range given by DLS, it is necessary to represent all data together to quantify the peptization time at which the transition between the starting large agglomerates and the small particles or groups of few particles resulting after peptization occurs. This transition region defines the peptization time in a more accurate way than has ever been reported, to the best of our knowledge.

The same procedure has been done for sols synthesized at different temperatures ranging from 25 to 80 °C. The peptization times have been defined as the time where the mismatch between the two experimental techniques takes place (i.e., the “drop time”) that ensures that peptization has finished. In Figure 4, the peptization time estimated for sols synthesized at different temperatures is plotted. As it is observed, sols prepared at 25 °C present a peptization time of ~95 h, sols prepared at 30 °C need ~72 h for a complete peptization, sols synthesized at 35 °C present a peptization time of ~45 h, those prepared at 50 °C show a peptization time of ~9 h and those prepared at 80 °C need a peptiza-

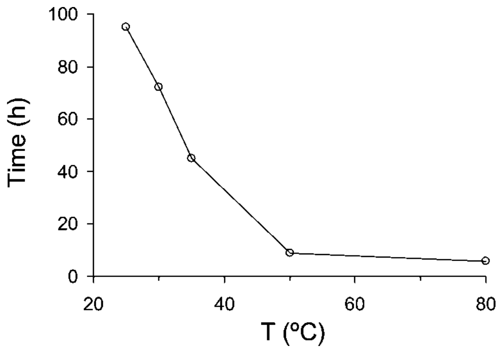

Figure 4. Evolution of peptization time as a function of synthesis temperature.

tion time of ~6 h. The peptization time for sols prepared above 80 °C is even shorter and the synthesis is less reproducible and the risk of uncontrolled gelation increases, hindering the sol manipulation. Because particle size decreases with decreasing peptization temperature, it is favorable to peptize titania sols at low temperatures, so that it is recommended, under the synthesis conditions used in this study, to synthesize the sol at temperatures of 25 °C.

The average particle size is not affected by ionic strength of the medium (i.e., the surface charge around the particles) since equal HNO_3 concentrations were used. Thus, it is believed that the TiO_2 particle size depends on peptization temperature. A higher peptization temperature implies a higher thermal energy (kT) and results in breaking the agglomerates during peptization. But there is limit to this behavior, as an excess of thermal energy can promote diffusion of particles and overcome the electrostatic repulsion, resulting in agglomeration. This limit seems to depend on the synthesis conditions, for instance Mohammadi et al.[6] found its temperature limit between 50 and 70 °C. In our study above 25 °C, the TiO_2 average agglomerate size increases with synthesis temperature.

To evaluate the consistency of the proposed methodology to define the peptization time, we completed a new series of experiments, consisting of the continuous recording of the transmitted NIR light with peptization time at the same conditions used for laser diffraction and DLS determinations. Figure 5 shows the evolution of transmitted light percentages measured for a sol synthesized at 30 °C with reaction time. The average size values plotted in Figure 2 are also shown for easy comparison.

It can be observed that up to 40 h, light cannot transmit along the measuring cell because the suspension is opaque because of the presence of large agglomerates, as confirmed by the large size measured by laser diffraction. There is, however, a defined time, after 40 h, where transmission sharply increases, confirming that particles are so small that light can cross the cell, which is in perfect agreement with data obtained by particle size measurements, as this gap occurs at the same time after which the DLS technique starts to measure and diffraction gives no further data. The good correlation among the measurements obtained by the different techniques indicates that the proposed methodology is useful to quantify the time needed for peptization to occur.

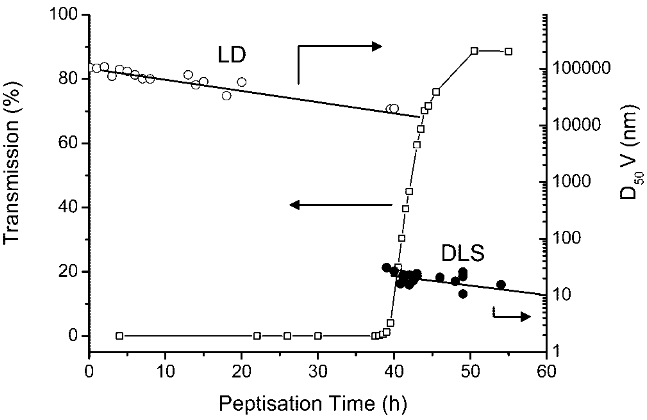

Figure 5. Near-infrared transmitted light measurements as a function of peptization time as compared with laser diffraction and DLS measurements. Sol synthesized at 30 °C.

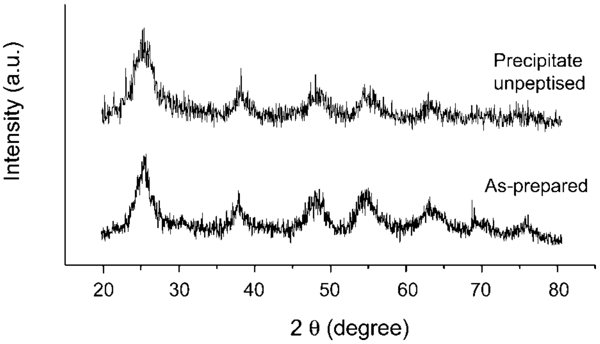

Figure 6. XRD patterns obtained for the precipitate formed after hydrolysis of the alkoxide (a) before peptization and (b) after peptization and drying for a sol synthesized at 30 °C.

The sols were found to be very stable in terms of viscosity and agglomerate size distribution: neither their particle size distribution nor their rheological properties changed for aging periods as long as 7200 h (10 months), showing always a Newtonian behavior with a viscosity of ~3 mPa s for all cases.

Xerogel Characterization. The as-prepared xerogel obtained from the sol synthesized at 30 °C was characterized in terms of surface area, XRD and TEM. Measured surface area was 159 ± 6 m^2/g after degassing at 150 °C. In Figure 6 the X-ray diffraction patterns of both the white precipitate obtained just after hydrolysis of the alkoxide and dried at room temperature without any further treatment (i.e., before peptization) and the as-synthesized xerogels (i.e., after peptization) are displayed. Anatase is obtained in both cases, although peaks are wide and poorly defined, as expected for nanoparticles. In Figure 7, the XRD patterns obtained for samples treated at temperatures up to 600 °C are shown. It can be observed that samples consist of anatase phase, stable up to 400 °C, and that rutile phase appears in samples treated at that temperature or above, and traces of anatase are still observed in samples treated up to 500 °C. Traces of brookite could be also present in both cases,[23] although it is not possible to make an unequivocal assignation since the

---

(23) Mohammadi, M. R.; Cordero-Cabrera, M. C.; Ghorbani, M.; Fray, D. J. *J. Sol-Gel Sci. Techn.* **2006**, *40*, 15.

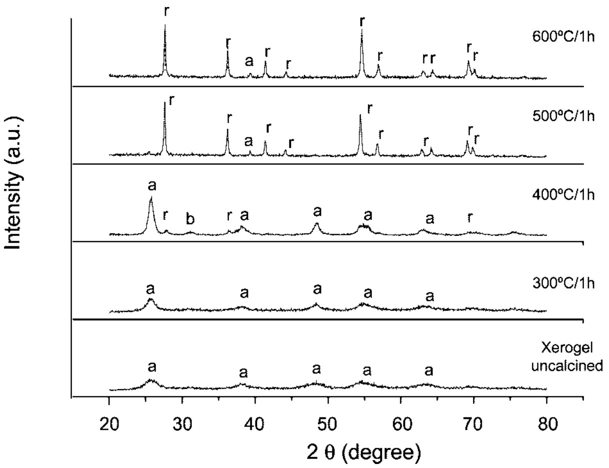

Figure 7. Diffraction patterns of the as-synthesized xerogel from a sol synthesised at (a) 30 °C and after heat treatments at (b) 300, (c) 400, (d) 500, and (e) 600 °C for 1 h.

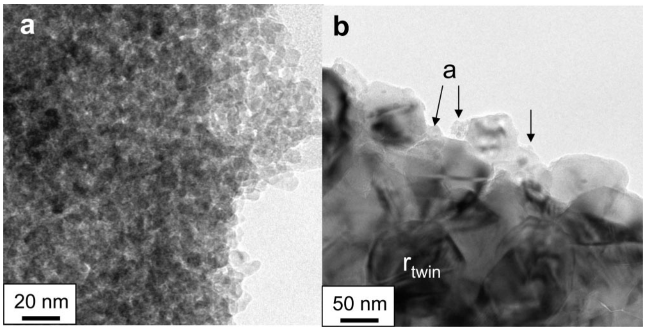

Figure 8. TEM microphotograps of xerogels obtained from a sol synthesized at 30 °C and calcined at (a) 300 and (b) 500 °C for 1 h.

intensity background is high. A small peak of brookite clearly appears at 400 °C and above this temperature is not longer observed.

In Figure 8 TEM microphotographs of a xerogel treated at (a) 300 and (b) 500 °C for 1 h are shown. In the former, it can be observed that primary particles have less than 10 nm, very close to the average particle size values obtained for the sols during the synthesis. This suggests that the synthesized sol is formed by agglomerated particles. Microphotographs of the xerogel calcined at 500 °C show two different crystallite sizes, a major fraction of bigger particles (~60−90 nm) and a minor fraction of smaller ones that have a slightly higher size than samples treated at 300 °C. Taking into account that both anatase and rutile phases are present (see the XRD pattern) in the xerogel calcined at 500 °C and being the rutile the predominant phase, we could assign the small crystals to the anatase phase and the bigger ones to the rutile phase. This is in agreement with Hu et al.[24] and Zhang et al.,[25] who proposed that a critical crystallite size (~14 nm) may exist for the anatase-rutile phase transformation. Below that size anatase would be favored. Rutile transformation would take place when crystallite size exceeds that value. Furthermore, in Figure 8b, rutile particles of ~50 nm that have an anatase particle close to them can be seen. Twin rutile particles can also be observed. These observations could be the result of the rutile particle growth and anatase−rutile transformation process described by Lee and Zuo.[26] Those authors studied the growth and transformation mechanism in nanometer-sized titania powders. In that process, once the rutile is nucleated, it grows fast by absorbing neighboring anatase particles. The absorption is accompanied by both the disappearance of anatase and the growth of rutile particles. Rutile grows until there are no anatase particles near the rutile particle. After cooling, rutile particles showed a twin structure, which was often observed in the coalesced rutile particles.

Conclusions

Different optical techniques have been used as "in situ" tools for following up the peptization process of a $TiO_2 \cdot xH_2O$ sol prepared by a particulate sol−gel route, i.e., laser diffraction (LD), dynamic light scattering (DLS), and multiple light scattering with a near-infrared light. The combination of the data measured with these techniques is useful to follow-up the evolution of the peptization process and to unequivocally establish its end. The peptization time is determined as the time for which an experimental mismatch between the measurements performed with the two laser techniques is found. This gap coincides also with a strong and sharp increase of the transmission of near-infrared light measured by turbidimetry. Peptization time significantly increases as the synthesis temperature decreases: Sols prepared at 25 °C present a peptization time of ~95 h, sols prepared at 30 °C need ~72 h for a complete peptization, sols synthesized at 35 °C present a peptization time of ~45 h and those prepared at 50 °C show a peptization time of ~9 h. The peptization time for sols prepared above 80 °C is quite short and the synthesis is less reproducible and the risk of uncontrolled gelation increases. The average particle size changes from ~13 nm for sols prepared at 25 °C, to 20 nm for sols prepared at 35 °C and, to ~30 nm for sols prepared at 50 °C. Although this article deals with the compliance of peptization process in order to control the steps for the synthesis of nanoparticulate $TiO_2 \cdot xH_2O$ sols, the proposed methodology is expected to apply to other metal oxide sols prepared by particulate sol−gel routes.

Acknowledgment. This work has been supported by the Spanish Ministry of Education and Science (MAT2006-01038) and the Interuniversity Attraction Poles Program (P6/17)-Belgian State-Belgian Science Policy.

CM703560X

---

(24) Hu, Y.; Tsai, H.-L.; Huang, C.-L. *Mater. Sci. Eng., A* **2003**, *344* (1−2), 209.

(25) Zhang, H.; Banfield, J. F. *J. Mater. Chem.* **1998**, *8* (9), 2073.

(26) Lee, G. H.; Zuo, J-M. *J. Am. Ceram. Soc.* **2004**, *87* (3), 473.