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Preparation and Characterization of Colloidal Solution Derived Crystallized Titania Powder

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Abstract

In this work the influence of the type of the titanium alkoxide and the type and concentration of the peptizing agent on the powder crystallization is pointed out. Anatase or rutile phases are directly precipitated from the sol during ageing in case of the use of hydrochloric or nitric acid as peptizing agent. If tetraethylammonium hydroxide is used the sol is very stable and an amorphous powder is only obtained after drying at 100°C. The sols and obtained powders were characterized. Dans ce travail nous avons étudié l'influence de la concentration et de la nature de l'agent peptisant ainsi que celle de l'alkoxyde de titane sur la cristallisation de la poudre. En utilisant les acides nitrique et chlorhydrique comme agents peptisants, on obtient une poudre cristallisée sous la forme anatase ou rutile. Si on utilise l'hydroxyde de tétraethylammonium le sol obtenu est très stable, la poudre récupérée après séchage à 100°C est amorphe. Les sols et les poudres obtenues sont caractérisés.

1 Introduction

Titania synthesized by sol–gel process can be used, for instance, as membrane material[1–3] and catalysis material.[4] The advantages of the method described in this paper are: (i) obtaining of powders for membrane preparation avoiding the amorphous-crystalline state transition; (ii) obtaining of crystallized powders with high specific surface area.

It is well-known that the sol–gel process derived materials are strongly influenced by all the parameters of this process. In the case of a colloidal route the nature of the material precursors and the peptizing agents must be, particularly, taken into account. The crystallization and the morphology of the materials depend on the preparation conditions of the sol. Usually, a sol, depending on its stability, leads to a gel or an amorphous precipitate. In this work, titania crystallized powder was directly obtained from a colloidal sol if acid is used for the peptization.

The goal of this study is to point out the influence of nitric acid concentration on the crystallization of titania from precipitated hydrous titanium oxide obtained[5–7] by complete hydrolysis of an alkoxide. A comparison of the results using nitric acid, hydrochloric acid and tetraetylammonium hydroxide as peptizing agent was performed. The influence of the nature of the alkoxide using nitric acid as peptizing agent was noted.

2 Experimental

Titania sol was prepared by the following way. Hydrous titanium oxide was precipitated by adding titanium alkoxide in water (18 MΩ) under magnetic stirring which is maintained during all the time of the experiment. Nitric acid was added when the suspension is very homogeneous, the mixture has the following composition: 22·5 g of water; 7 g of alkoxide [titanium tetraisopropoxide: $Ti(OiPr)_4$]; 10·5 g of HNO_3 (x M), x varies from 1 to 11.

The HNO_3 concentration in the mixture was varied from 0·25 to 2·75 M. The aspect of solutions are reported in Table 1. The water quantity corresponds to an hydrolysis ratio of alkoxide equal to 50.

At this time, the suspension was heated at 60°C and this temperature was maintained about 24 h.

In a first step, the peptization time, determined by the appearance of a homogeneous opaque solution, has been measured. Then, the colloidal

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Table 1. Evolution and aspect of solutions

Powder number	*Solution number*										
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*
$[HNO_3]$ (M)	0·25	0·37	0·5	0·62	0·75	0·87	1	1·25	1·75	2·5	2·75
Peptization time (min)	65	50	45	30	20	10	8	5	< 5	< 5	< 5
Aspect of solutions	SS	SS + D	SS + D	SS + D	SS + D	SS + D	SS + D	SS + D	D	D	D

SS, stable solution; D, settling.

particle size was determined by granulometry (Horiba Capa 700) and the turbidity of the sols was measured (Hach Turbidimeter Ratio/XR). Precipitation time was noted when a settling appears.

Titania sols were dried in an oven at 100°C and crushed to reduce aggregates. The powder characterization was performed using scanning electron microscopy (SEM Hitachi S4500), X-ray diffraction (Inel CPS-120), infrared spectroscopy (FTIR Nicolet ZDX), thermal analysis (TGA apparatus made in laboratory, DTA Netzsch 404) and N_2 adsorption (Micromeritics ASAP 2000).

3 Results

3.1 Study of solutions

3.1.1 Time of peptization

The peptization time was measured from the addition of HNO_3 in the suspension. It decreases when the acid concentration is increasing (Fig. 1). Precipitation time varies by the same way as peptization time but it is very difficult to determine it because of the very low turbidity in certain cases for the lowest acid concentrations. If the HNO_3 concentration is higher than 1·8 M, the time of peptization and precipitation are very short (less than 5 min).

3.1.2 Particle size

The general variation of the particle size versus the acid concentration can be observed on Fig. 2. A double distribution is observed. For lowest acid concentrations, till 0·75 M, the first grain size distribution is centered on 0·1 μm, the second one increases with $[HNO_3]$ from 0·01 to 0·05 μm. The amount of 0·1 μm sized particle proportion increases from 0·25 to 0·875 M, value for which the maximum is reached. For higher acid concentration, this proportion decreases and the particle size distribution is broader around 0·5 μm; another grain size distribution is centered on 1 μm. For $[HNO_3]$ equals 2·5 and 2·75 M, a very small amount of 0·01 μm sized particles appears also.

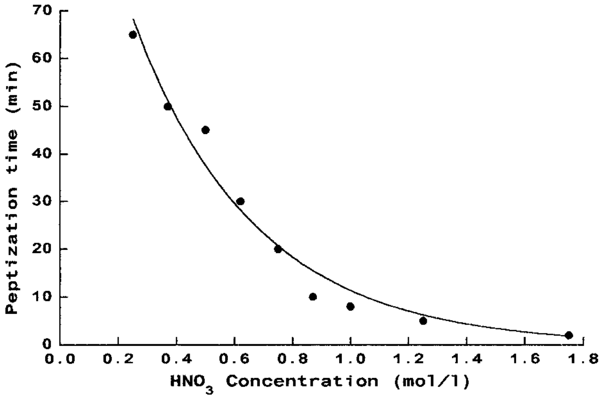


Fig. 1. Peptization time versus HNO_3 concentration.

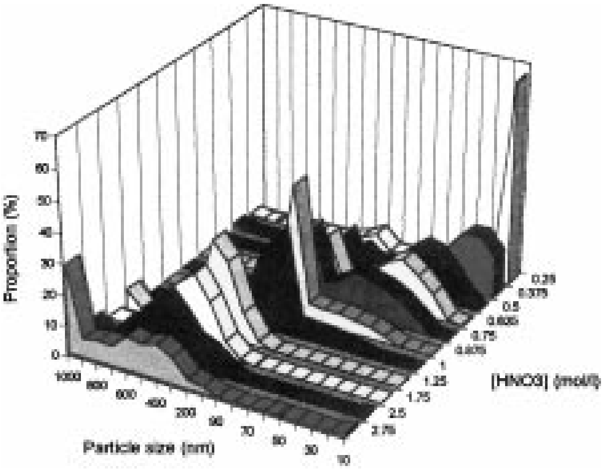


Fig. 2. Particle size versus HNO_3 concentration.

3.1.3 Turbidity measurement

The turbidity of the solutions was measured after dilution by a factor of 100. Highest values of turbidity were obtained for acid concentration from 0·875 to 2·75 M with a maximum at 1·25 M (Fig. 3).

3.2 Study of powders after drying at 100°C

3.2.1 X-ray diffraction

The evolution (Fig. 4) of the intensities of the (101) reflection of anatase and the (110) reflection of rutile, respectively, is a function of nitric acid concentration for different solutions. It can be observed that, at the two ends of the acid concentration scale, the main form which appears is

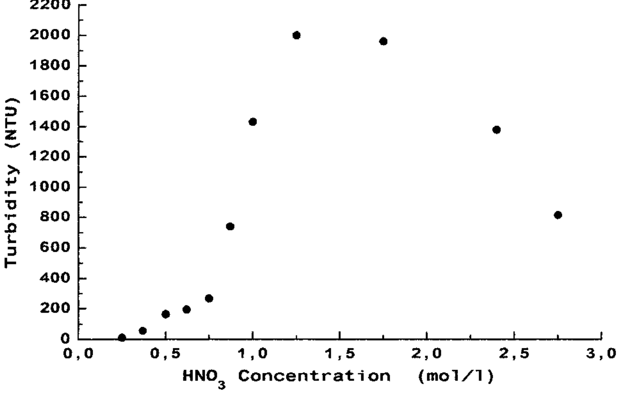


Fig. 3. Turbidity versus HNO_3 concentration.

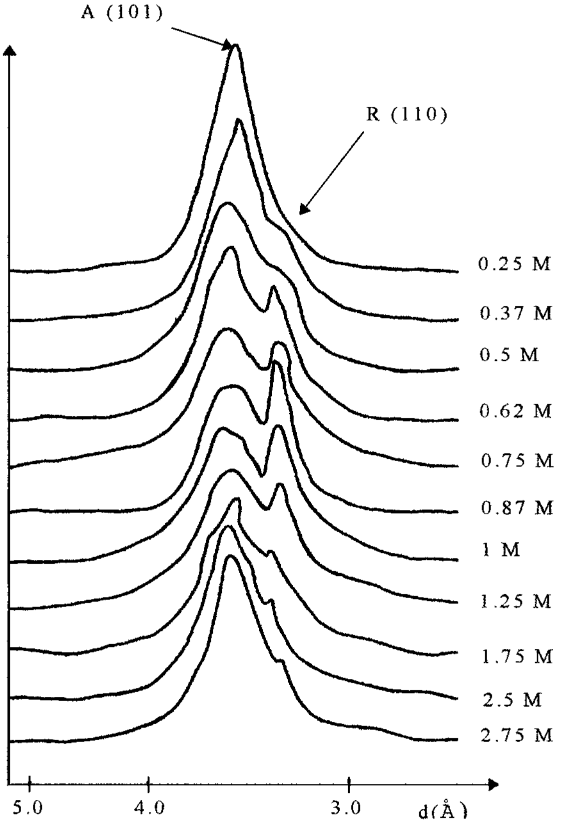


Fig. 4. XRD patterns of titania powder, prepared with different concentrations of HNO_3.

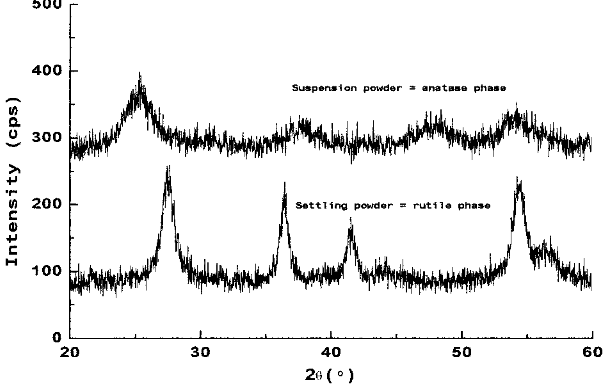


Fig. 5. XRD patterns of the settling and suspension powders.

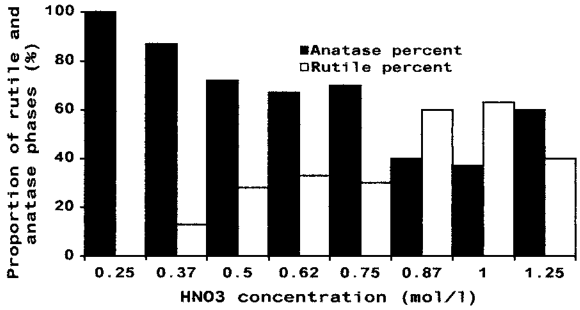


Fig. 6. Proportion of rutile and anatase phases versus HNO_3 concentration.

the anatase form, in great proportion for $[HNO_3] = 2{\cdot}75\,M$ and exclusively for $[HNO_3] = 0{\cdot}25\,M$. Except for this last concentration, rutile form has been found with a maximum for 0·875 and 1 M nitric acid solutions.

After centrifugation at 5000 r min^{-1} for 3 h, settling and suspended colloidal particles were separately dried at 100°C. X-ray diffraction patterns (Fig. 5) show that the settling powder is in the rutile phase and the suspended powder is in the anatase phase.

By weighting the powders, the proportion of rutile and anatase phases was determined and reported in Fig. 6. For the highest acid concentration (1·75 to 2·75 M) it can be observed by comparison of the different patterns on Fig. 4 that anatase phase proportion is about 90%. It is impossible to separate anatase and rutile phases by centrifugation because of settling of the two phases. The sol of anatase is very unstable due to a screening of the electrostatic repulsion between colloidal particles. Rutile phase was not observed by X-ray diffraction for the lowest acid concentration.

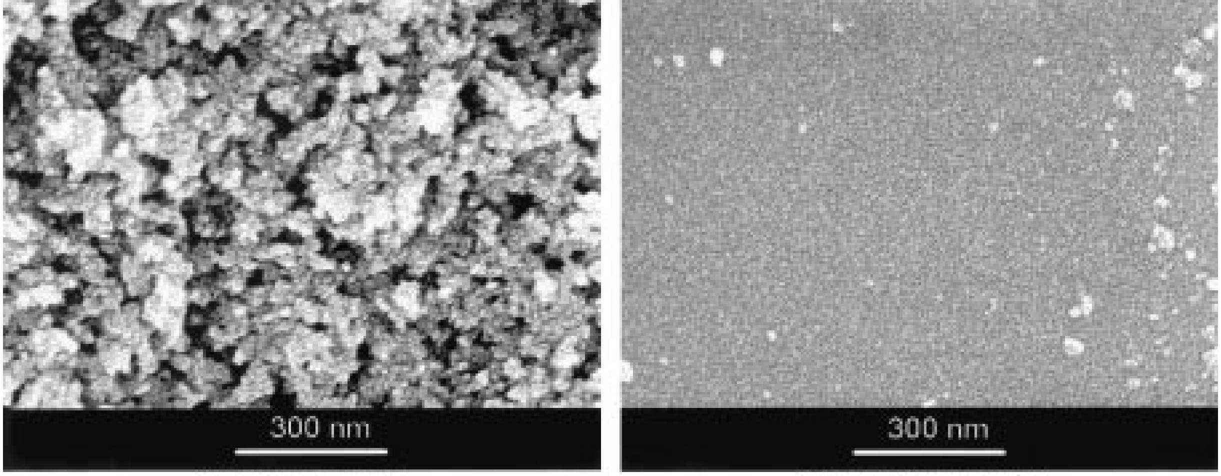
3.2.2 Surface area and morphological aspect

The specific surface area were measured on 200°C degassed powders. Surface area is $320\,m^2\,g^{-1}$ for suspension powder and $120\,m^2 g^{-1}$ for settling powder. These results are verified by SEM analysis in Fig. 7. On these micrographs the difference in particle size is easily pointed out.

3.3 Study of powders after firing

3.3.1 X-ray diffraction

The evolution of crystallization was controlled after firing of the powders 1 and 6 by XRD; for powder 1 (Fig. 8), rutile phase appears from 300°C and the transformation is complete at 600°C. For powder 6 (Fig. 9), despite the fact that, at 100°C, rutile phase is the main phase, the complete transformation from anatase to rutile is complete at the same temperature than powder 1.



Settling powder

Suspension powder

Fig. 7. Morphological aspect of the settling powder and the suspension powder.

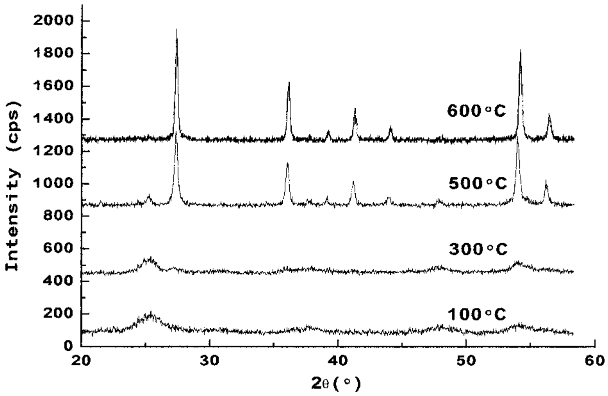


Fig. 8. XRD patterns of powder 1 after treatment at different temperature.

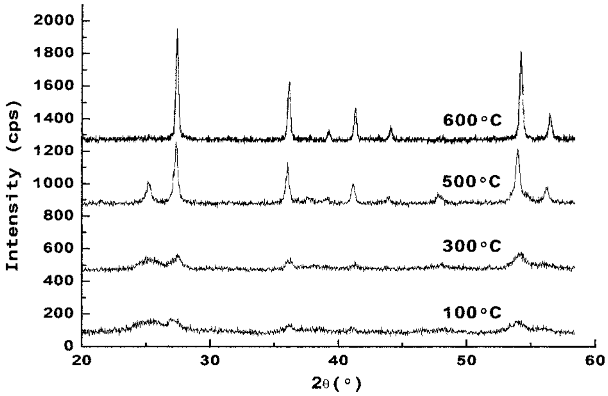


Fig. 9. XRD patterns of powder 6 after treatment at different temperature.

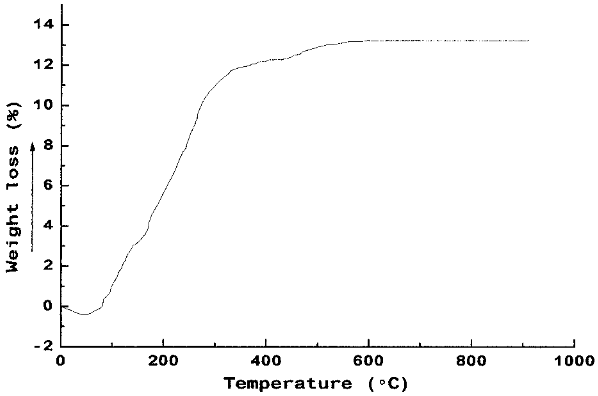


Fig. 10. TGA curve of powder 7, heating rate 5°C min^{-1}.

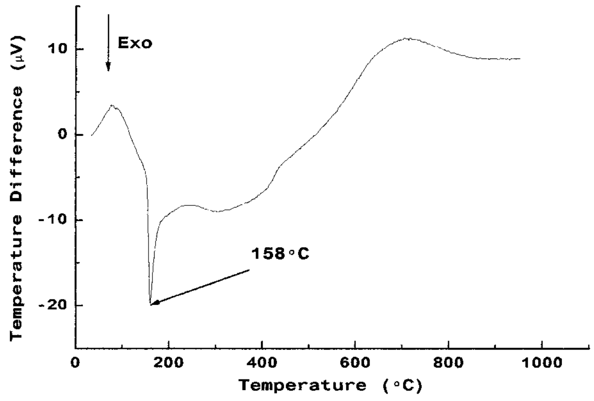


Fig. 11. DTA curve of powder 7, heating rate 5°C min^{-1}.

3.3.2 Thermal analysis

Figure 10 shows the TGA (thermogravimetric analysis) curve of TiO_2 powder. This curve essentially shows that the complete weight loss of this sample occurred between 100 and 500°C. This weight loss is due to the removal of water and nitric acid. An exothermic peak on the DTA (differential thermal analysis) curve can be observed (Fig. 11). This phenomenon observed in TGA and DTA is due to the decomposition of the nitrates. This was verified by FTIR spectroscopy. Figure 12 shows the IR spectra of the dry powder at 100°C together with the calcined powder at 200°C. During the calcination the NO_3^- is removed, as it is indicated by the disappearance of the asymmetric stretching band of NO_3^- ion at 1383 cm^{-1}.

Similar TGA, DTA and FTIR curves are observed for all TiO_2 powders.

3.3.3 Morphological aspect

Powders 1, 6 and 11, were examined by Scanning Electron Microscopy after calcination at 200°C for 5 h. Figure 13(a) and (c) shows a similar morphological aspect (the two powders are in the anatase phase). Figure 13(b) is different, it is less compact, it shows similar aggregates to the rutile form in Fig. 7.

4 Discussion

Depending on nitric acid concentration pure anatase or mixture of anatase and rutile can be obtained. In all cases anatase powders are finer than rutile powders. This can be observed with the various results of characterization.

The relative proportion of anatase can be related to:

- the aspect of the solution; settling part corresponds to the rutile phase;
- the size of the particles (lower for anatase phase);
- the turbidity which decreases when anatase proportion increases;
- the specific surface area, which is higher for anatase than for rutile.

Other peptizing agents were also used to peptize hydrous oxide precipitated from the same alkoxide under the same conditions. Firstly hydrochloric acid was used at two concentrations: 0·75 M for powder 1HCl and 0·875 M for powder 2HCl.

Table 2 shows that the peptization time decreases when HCl concentration increases. The aspect of solutions peptized with HCl are like the aspect of solutions prepared with the highest nitric acid concentrations.

Crystalline phases of powders as a function of HCl concentration are given in Fig. 14. Powder 1HCl, is in the rutile and anatase phase, with a large proportion of rutile. Powder 2HCl is in the rutile phase.

Figure 15 shows SEM micrographs of both powders. In the powder 1HCl we can see large agglomerates (mixture of anatase and rutile). In powder 2HCl we can see rod shaped particles in rutile phase. These results are verified from the values of specific surface area, 153 m^2 g^{-1}, for powder 1HCl and 132 m^2 g^{-1} for powder 2HCl.

The use of HCl instead of HNO$_3$ increases the crystallization of rutile which is the only

Table 2. Evolution and aspect of solution

	[HCl]M	*Peptisation time (min)*	*Solution aspect*
Solution and powder 1HCl	0·75	20	Settling
Solution and powder 2HCl	0·875	15	Settling

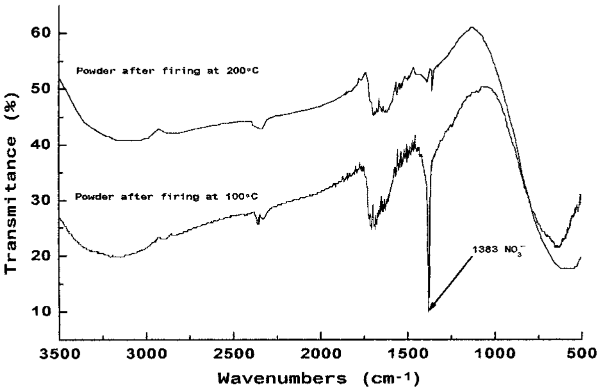


Fig. 12. FTIR spectroscopy of powder dried in an oven at 100°C and a powder calcined at 200°C during 2 h.

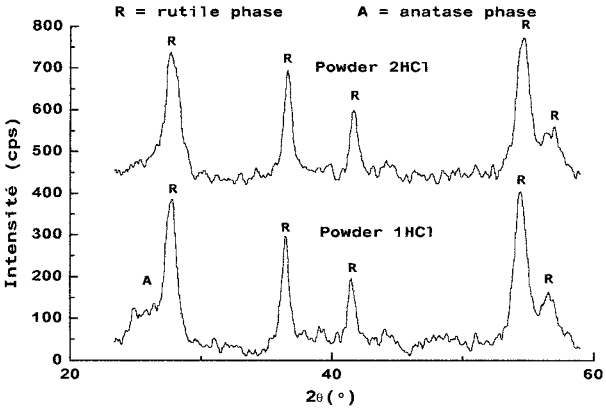
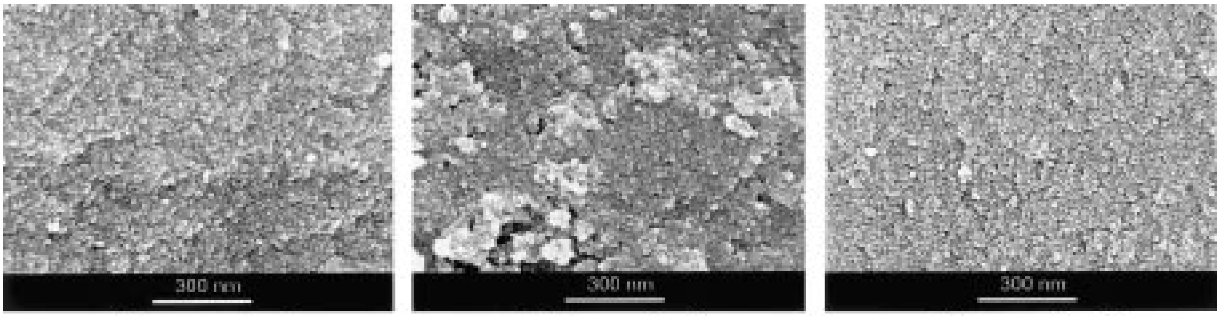
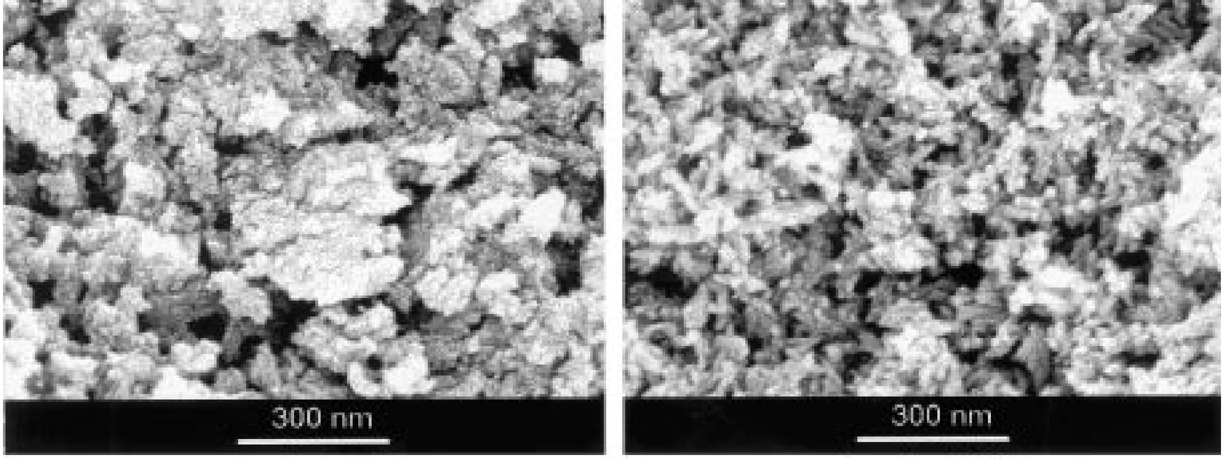


Fig. 14. XRD patterns of powders 1HCl and 2HCl.



13a powder 1   13b powder 6   13c powder 11

Fig. 13. Micrographs of powders 1, 6 and 11.



Powder 1HCl Powder 2HCl

Fig. 15. Micrographs of powders 1HCl and 2HCl.

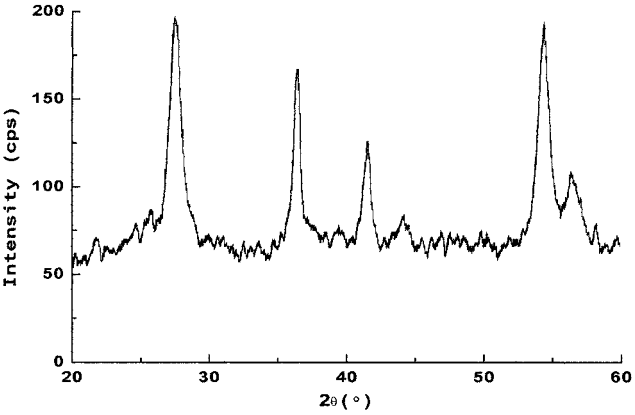


Fig. 16. XRD pattern of titania sol dried at 100°C.

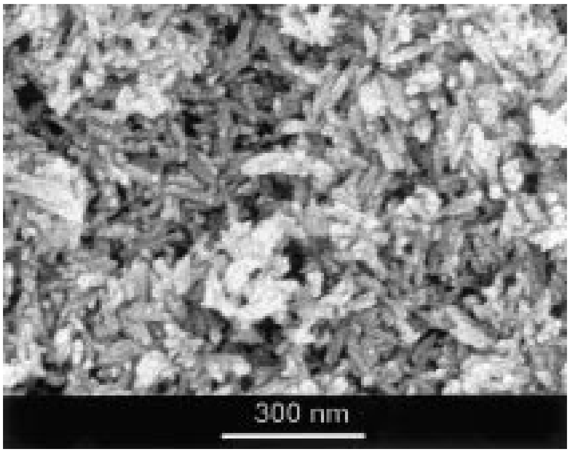


Fig. 17. Micrograph of powder prepared with tetrabutyl orthotitanate.

crystallized phase on acid concentration equal to 0·875 M.

Secondly, tetraetylammonium hydroxide was used for peptization. One test was performed with a base concentration equal to 0·45 M. The peptization led to a very stable colloidal solution and no precipitate appears. The solution was dried at 100°C in an oven, the powder obtained was analyzed by X-ray diffraction and found to be amorphous.

Finally, titanium tetrabutoxide was used as precursor of precipitated hydrous oxide and nitric acid at a concentration equal to 1·25 M was added for peptization which occurs after 5 min; the precipitation takes place 5 min later. XRD analysis of powder (Fig. 16) shows that the titanium is in the rutile form. Figure 17 shows the micrograph of powder prepared with titanium tetrabutoxide.

The difference between these results and those obtained with TI(OiPr)$_4$ are in the rutile content and grain morphology, grains are aggregated to form rods.

5 Conclusion

The various results obtained in this study confirm that the control of the experimental conditions are preponderant for the characteristics of the obtained powder. If the peptizing agent is a mineral acid, the powder precipitated from the colloidal solution is crystallized and the crystalline phase depend on the nature of the alkoxide and on the nature and the concentration of the acid. If a base is used as peptizing agent, the 100°C dried gel is amorphous. The specific surface area of anatase and rutile phases are high and correspond at the particle sizes equal to 5 and 12 nm, respectively.

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