JOURNAL OF MATERIALS SCIENCE **34** (1999) 3397–3404

Preparation of nanometric titanium hydrous oxide particles by vapour phase hydrolysis of titanium tetrabutoxide

F. RUBIO, J. RUBIO, P. DURAN, J. L. OTEO
Instituto de Cerámica y Vidrio. C.S.I.C., 28500 Arganda del Rey, Madrid, Spain
E-mail: frubio@icv.csic.es

Spherical titanium nanoparticles in the range of 60 to 500 nm have been obtained by a vapour-phase hydrolysis procedure using titanium tetrabutoxide as raw material. In this work, different parameters such as alkoxide temperature, water temperature, carrier gas flow rate, inlet pressure, vacuum and dilution of the raw material were tested. The most important parameters in order to obtain nanoparticles of low mean size were the flow rate, the alkoxide temperature and the inlet pressure. When the temperature decreases the mean size decreases obtaining nanoparticles below 100 nm when the temperature is set up to 125 °C. On the other hand, as the flow rate that pass through the alkoxide increases the particle size decreases. Same behaviour is observed when the pressure inlet is increased. In all cases, these results are attributed to a minor concentration of the alkoxide (low amount of alkoxide molecules) in the gas stream. The other parameters, vacuum, water temperature and dilution of the alkoxide did not show any important influence in the particle size as the other ones. Polydispersity (broad or narrow particle size distribution) has the same trend. The alkoxide temperature and carrier flow rate generate narrow distributions while the other parameters produces broad distributions. FT-IR analysis of these nanoparticles showed that for sizes below 100 nm the alkoxide is fully hydrolysed and as the particle size increases the nanoparticle has more alkoxide or alcohol retained inside. The heat treatment of these nanoparticles produces a decreasing in the particle size and in all cases, the spherical shape is retained and no blackening in the nanoparticles of higher size is observed. *© 1999 Kluwer Academic Publishers*

1. Introduction

Several techniques are widely applicable to obtain an enormous variety of materials in the form of submicron spherical particles. SiO_2, TiO_2, ZrO_2, ZrO_2-Al_2O_3, ZnO, Fe_2O_3, V_2O_5, etc. can be obtained as they are described in a series of excellent reviews [1–4]. In the last years, the need for high technology ceramic materials has led to the idea that an uniform particle size facilitate the preparation of high dense powder compacts and therefore the best sintering behaviour. However, it is now recognised that for sintering to high density it is more important to have a uniform pore size distribution in the green body. On the other hand, a denser body can be made with a wide range of particle size. Ring [5] has obtained the higher density materials by using materials with a variation in particle size in the range of 10 to 30%.

Titanium oxide powders have been studied extensively due to its applications as photoconductor, pigments, coatings and fillers [6–11]. In a previous paper [12] we have characterised the behaviour of submicron spherical titanium hydrous oxide particles obtained by vapour-phase hydrolysis of titanium tetrabutoxide (TTB) as well as the green and sintered compacts obtained by using such submicron particles. This experimental method allows the preparation of particles with different particle sizes by changing the experimental conditions. Spherical particle sizes below 100 nm and above 1000 nm can be obtained by this method. In the present work we show the different particle size distributions which can be obtained when the vapour-phase hydrolysis procedure is used. In this procedure, TTB has been used as starting material in order to obtain titanium oxide powders. We have also studied the degree of hydrolysis of the TTB as a function of the particle size of the as-prepared powder.

2. Experimental

2.1. Materials

TTB (Fluka, 99% purity, 1% *n*-butanol) and double distilled-deionized water were used as starting materials. The presence of *n*-butanol in the TTB is necessary because pure TTB is a highly hydrolyzable solid. Nitrogen (99.999% purity) was used as carrier gas. In some experiments ethanol (EtOH), *n*-propanol (*n*-PrOH) and *n*-butanol (*n*-BuOH), all of them Merck for analysis, were used mixed with the carrier gas.

0022–2461

2.2. Vapour-phase hydrolysis and particle formation

In principle, the technique consist of the evaporation of TTB at a given temperature. The TTB vapours are carried by nitrogen gas to the hydrolysis chamber where water vapour is also carried by another stream of nitrogen gas. The obtained particles are taken to a microfilter where are collected. This apparatus is schematically represented in Fig. 1. Dry nitrogen supplied by a tank and controlled by a manometer pass through a needle valve where the total flow and pressure of carrier gas are also controlled. This flow is divided into three, all of them controlled also by needle valves and passing independently through three glass containers where TTB, water or alcohol are present. These containers are heated (±0.1 °C) independently by thermostatic baths to the desired temperature. These streams are sprayed through gas nozzles with several holes of about 400 μm in diameter into the hydrolysis chamber. The hydrous titanium oxide particles formed in the hydrolysis chamber are taken to the collecting chamber where a Millipore filter of 150 nm of pore size is used. The system outlet is connected to a vacuum pump where different underpressures are applied.

The results showed in the present work deals with different experiments where inlet pressure, inlet flow, bath temperatures, alcohol mixing and vacuum system are tested. Table I gives such experimental conditions.

TABLE I Experimental conditions

Experience number	*Tb* (°C)	*Tw* (°C)	P N$_2$ (atm.)	Vacuum (mm Hg)	Flow rate (ml/min)	Alcohol
1	200	60	1.5	—	120	—
2	175	60	1.5	—	120	—
3	150	60	1.5	—	120	—
4	125	60	1.5	—	120	—
5	200	60	1.5	25	120	—
6	200	60	1.5	50	120	—
7	200	60	1.5	100	120	—
8	200	60	1.5	150	120	—
9	200	75	1.5	—	120	—
10	200	45	1.5	—	120	—
11	125	60	1.5	100	100	—
12	125	60	1.5	100	120	—
13	125	60	1.5	100	140	—
14	125	60	1.5	100	160	—
15	175	60	1.5	100	120	Ethanol
16	175	60	1.5	100	120	*n*-Propanol
17	175	60	1.5	100	120	*n*-Butanol
18	150	60	1.2	100	120	—
19	150	60	1.5	100	120	—
20	150	60	2.0	100	120	—
21	150	60	3.0	100	120	—

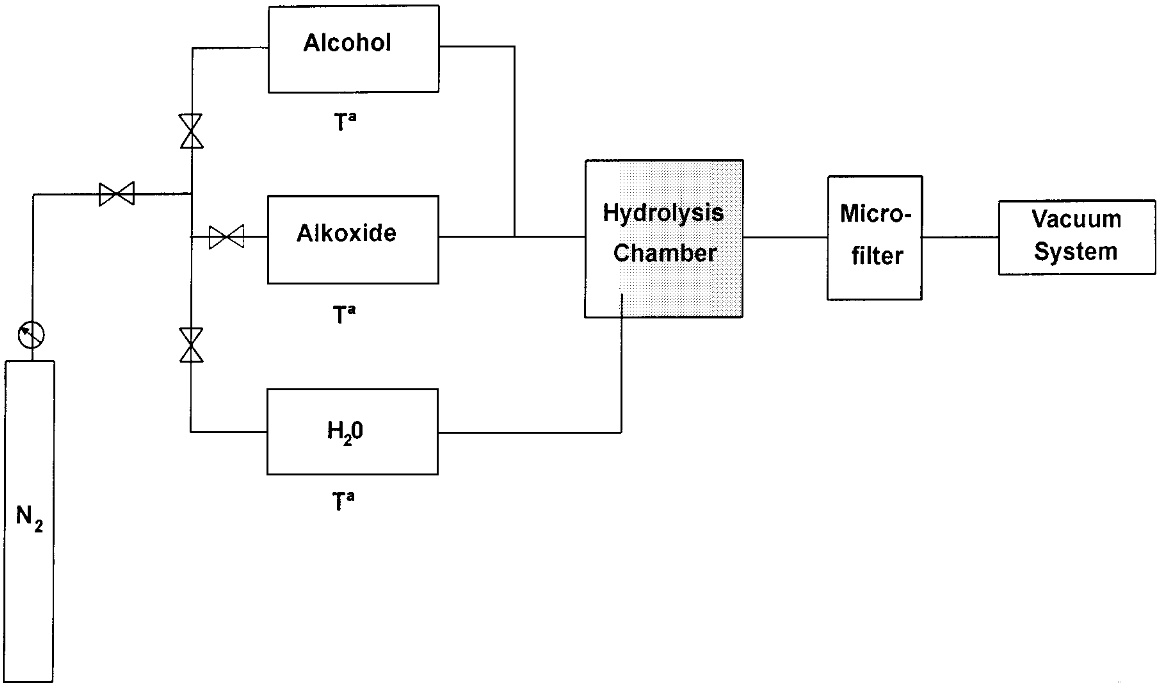


Figure 1 Vapour-phase system used for obtaining titanium nanoparticles.

2.3. Calcination

The powders prepared as described above were dried at 50 °C and the calcined in an oven at room atmosphere. The heating treatment was 1000 °C for 1 hour at a heating rate of 10 °C/min. In all cases spherical morphology was retained.

2.4. Particle characterisation

The particles collected in the microfilter were dried in an oven at 50 °C (±0.5 °C) for 24 hours and then studied by Scanning Electron Microscopy (SEM, Carl Zeiss DSM-950) and by Infrared Spectroscopy (FT-IR, Perkin-Elmer 1760X). Particle size distributions (PSDs) were determined by image analysis from SEM photographs for the as-prepared and calcined particles. At least 500 measured particles were used to determine the corresponding PSD. All PSDs were characterised by the statistic parameters: mean and median diameters (d and d_m respectively), standard deviation (σ) and monodispersity (σ^*, where $\sigma^* = 1 + \sigma/d$) [13]. FT-IR spectra were obtained by the KBr pellet method. 10 scans were used for each spectrum with a resolution of 2 cm^{-1}.

3. Results and discussion

Particle formation takes place instantaneously when the aqueous stream interacts with the TTB stream. This is observed by a sudden "fog" in the hydrolysis chamber. This "fog" is difficult to observe visually when PSD has an average spherical diameter below 100 nm. In this case, as in the others, the particles are collected in the microfilter. As we have said above, various studies were made in order to investigate the influence of several experimental conditions on the PSDs of the obtained titanium hydrous oxide particles. The experiments were carried out by varying one experimental condition and fixing the other ones. In all cases, the particles were smooth and spherical as can be observed in Fig. 2.

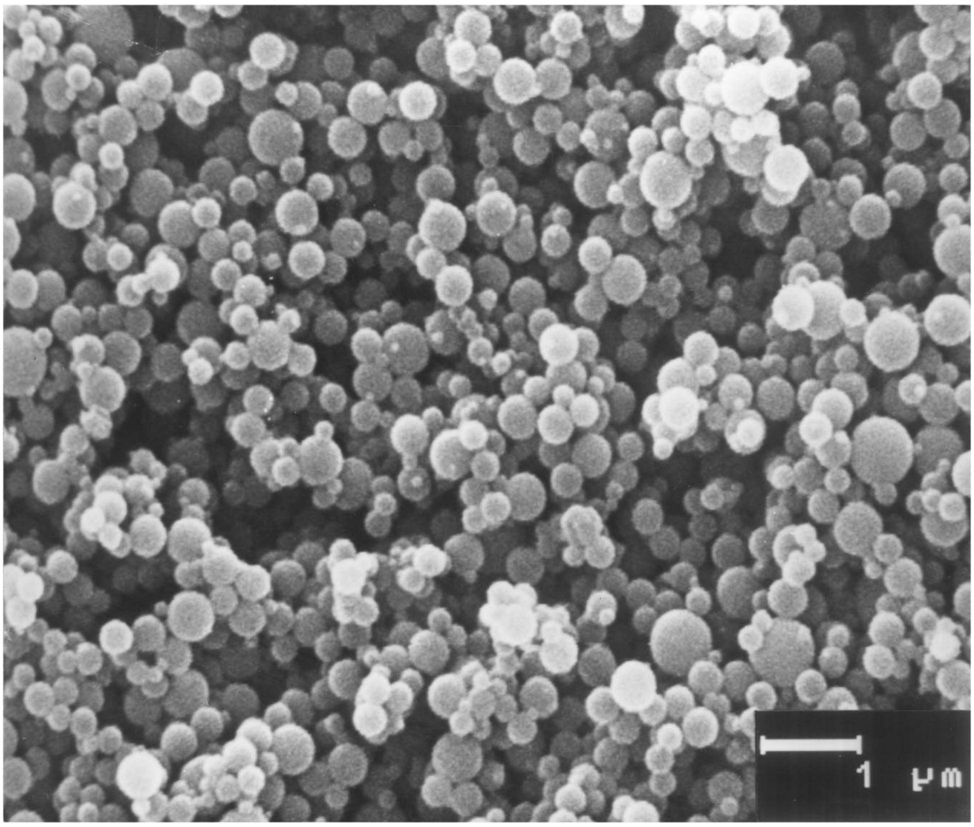
3.1. Particle size analysis

3.1.1. Influence of the TTB temperature

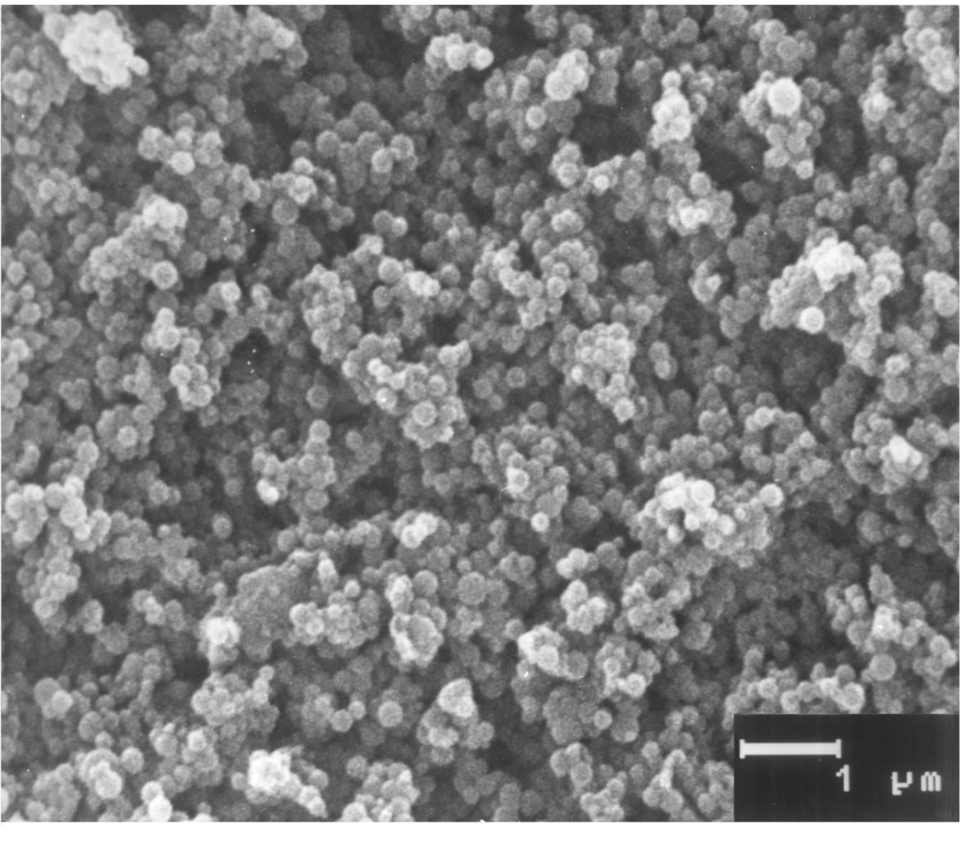
The experimental conditions are given in Table I, numbers 1–4. TTB is a viscous liquid with a boiling point of 310–314 °C at 1 atmosphere. Therefore if a dry carrier gas pass through a bath containing TTB at a given temperature lower than that, then the carrier gas stream will be saturated by TTB vapours at the corresponding partial pressure. Decreasing the TTB bath temperature decreases the TTB partial pressure and the carrier gas will have less TTB molecules. Fig. 3 shows the variation of the median particle size (d_m) of the PSDs obtained at different bath temperatures for the as-prepared and heat treated titanium hydrous oxide particles. It is observed, in this Fig. 3, that particle size distributions with median diameters below 100 nm can be obtained at bath temperatures lower than 125 °C. Mean diameters (assuming gaussian distributions) and standard deviations are given in Table II for the as prepared and heat treated samples. The standard deviation also decreases when the bath temperature decreases indicating that narrow PSDs are obtained at lower bath temperatures. However, monodisperse distributions are only obtained for PSDs prepared at 125 and 150 °C ($\sigma^* < 1.25$). Polydispersity increases as the particle size increases. Mean and median particle size also decrease when particles are calcined at 1000 °C. This result is due to the particle shrinkage that produce a decreasing in the specific surface area and porosity (1). PSDs close to 100 nm are obtained for particles obtained at 150 °C of bath temperature and calcined at 1000 °C.

TABLE II Mean diameters (d), standard deviations (σ) and polydispersity (σ^*) of the PSDs

Experience number	As prepared			Heat treated		
	d (nm)	σ (nm)	σ^*	d (nm)	σ (nm)	σ^*
1	515	232	1.45	485	237	1.49
2	302	83	1.27	252	80	1.32
3	153	34	1.22	138	30	1.22
4	76	16	1.21	74	16	1.21
5	464	259	1.56	414	170	1.41
6	428	222	1.52	425	183	1.43
7	434	286	1.66	406	191	1.47
8	524	299	1.57	489	263	1.53
9	510	229	1.45	489	252	1.51
10	525	226	1.43	508	264	1.52
11	92	20	1.22	96	20	1.21
12	81	18	1.22	75	16	1.21
13	68	14	1.20	67	15	1.22
14	60	12	1.20	60	12	1.20
15	224	74	1.33	205	68	1.33
16	209	76	1.36	202	71	1.35
17	201	75	1.37	188	67	1.36
18	184	46	1.25	173	50	1.26
19	156	36	1.23	145	33	1.23
20	146	44	1.30	137	36	1.26
21	124	46	1.37	110	30	1.27



(a)



(b)

Figure 2 Scanning electron microscopy of titanium nanoparticles: (a) experience 10 and (b) experience 12.

3.1.2. Influence of the vacuum in the system

In order to study the effect of the vacuum in the system we have selected the TTB bath temperature of 200 °C. The underpressures obtained with the aid of a vacuum pump are given in Table I, experiences 1 and 5–8. When vacuum is applied in the system, the particles obtained in the hydrolysis chamber are moving faster to the microfilter. Then, there exists a higher pressure drop

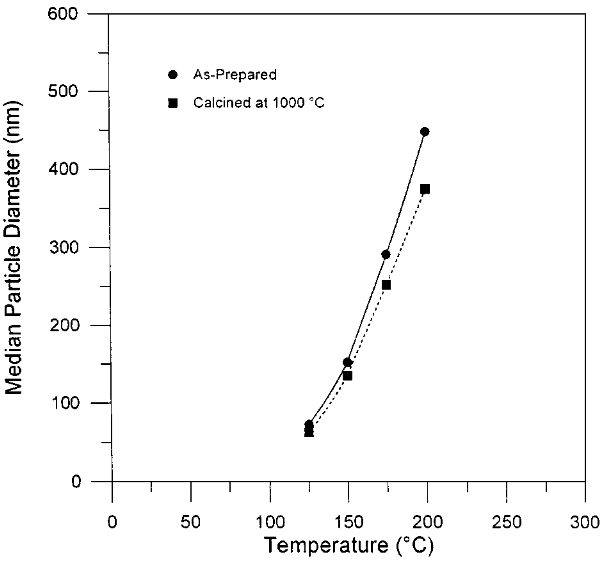


Figure 3 Influence of the Titanium tetrabutoxide bath temperature in the median particle diameter.

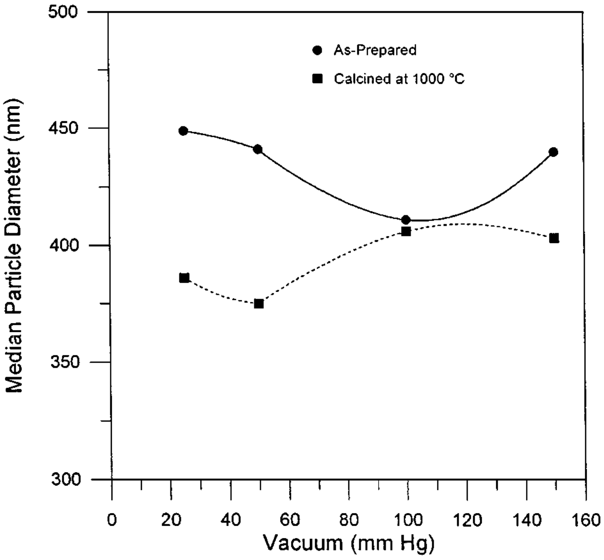


Figure 4 Influence of the vacuum in the median particle diameter.

between the glass nozzle and the hydrolysis chamber. This pressure drop can increase the spray effect making vapour TTB droplets of low size. In these experiments, the bath temperature of the hydrolysis water was set up to 60 °C (see Table I). Fig. 4 shows the variation of the median diameter of the PSDs for the different vacuum experiences. It seems that the vacuum system has no effect in the mean particle size because the obtained results are of the same order of magnitude. Statistical analysis was carried out by using the Statgraphics Programme, and the analysis of the variance of the different PSDs gives identical results for the four PSDs obtained when the vacuum in the system is modified. PSDs of the calcined samples did not show any change in the mean diameter, concluding that the vacuum has no influence in the PSD. Mean diameters and standard deviations of these PSDs are given in Table II.

On the other hand, vacuum seems to have influence on the polydispersity of the PSDs. Polydispersity increases as the vacuum increases, and this result corresponds to a high motion of the particles inside the hydrolysis chamber and the corresponding high probability of sticking between particles forming particles of higher mean size.

3.1.3. Influence of the water temperature

The influence of the water temperature was studied when TTB bath temperature was 200 °C and no vacuum in the system was used. Experimental conditions in Table I, numbers 1, 9, 10 correspond to these experiences. As the water temperature increases, the vapour partial pressure also increases and the hydrolysis stream will be more saturated in water. The studied water bath temperatures are given in Table I. For the water bath temperatures of 75, 60 and 45 °C, the median particle sizes obtained were 450, 448 and 435 nm respectively, and 408, 375 and 402 nm for the calcined samples. The statistical analysis of these PSDs did not show any differences between them. Table II gives also the mean diameter and the standard deviation of these PSDs. All of them can be considered as polydisperse and no influence on this polydispersity has the water bath temperature.

3.1.4. Influence of the carried gas flow

The speed of the carrier gas flow can be modified by the needles valves existing in the system. Since the water temperature did not have any effect in the particle size as we showed previously, then the carrier gas flow in the water bath was fixed to 12.5 ml/min and the carrier gas flow in the alkoxide bath was changed between 100 and 160 ml/min. The experimental conditions are given in Table I, numbers 11–14. Fig. 5 shows the influence of the carrier gas flow in the median particle size of the obtained PSDs. It can be observed, in this figure, that the median of the particle size decreases as the carrier gas flow increase. Calcined particles also show this behaviour, as can be observed in this Fig. 5. Table II also gives the mean diameter and the standard deviation of these PSDs. The obtained results are

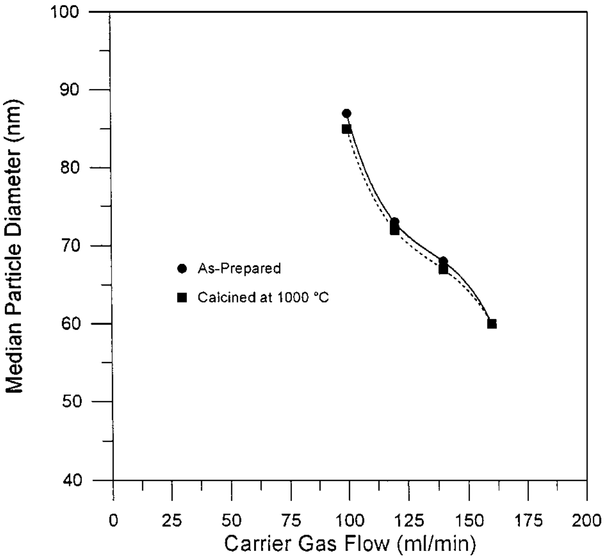


Figure 5 Influence of the carrier gas flow in the median particle diameter.

attributed to the difference in diameters between the glass nozzle and the hydrolysis chamber. This diameter difference produces an increasing in the pressure drop when the vapour alkoxide pass through the holes of the nozzle to the hydrolysis chamber, and therefore each vapour alkoxide droplet produces various droplets of lower size. Therefore, when the carrier gas flow is increased the glass nozzle works as a spray of the vapour alkoxide.

3.1.5. Influence of the mixing with alcohol vapours

As it was shown in Fig. 1, one of the three nitrogen streams can pass through a thermostatic bath where a liquid alcohol is present. This stream is then saturated with the corresponding vapour and injected into the vapour alkoxide stream before passing to the hydrolysis chamber. This procedure is implemented in order to prevent vapour alkoxide condensation during the short space which exists between the alkoxide bath and the hydrolysis chamber. The vapour alkoxide stream is then diluted by the vapour alcohols stream. Experiences were carried out by using EtOH, *n*-PrOH and *n*-BuOH as alcohols at the alkoxide bath temperature of 175 °C, as it is shown in Table I, experiences 15–17.

The obtained results by examining the PSDs showed a small decreasing in the median particle size diameter for both obtained and calcined samples. The measured median diameters for the experiments using EtOH, *n*-PrOH and *n*-BuOH were 210, 204 and 197 nm, respectively, and 201, 196 and 181 nm for the corresponding calcined samples. These values are below those of 291 and 248 nm for the as-prepared and calcined samples respectively, when no alcohol stream is used. A careful examination of the PSD by means of the analysis of variance using the Statgraphics Programme gave as a result that those distributions were analogous within a confidence level of 95%. It is necessary to count and measure a high quantity of particles in order to determine whether the alcohol stream has any influence in the particle size.

Polydispersity seems to be not influenced by the presence of the alcohol stream flow, as can be observed in Table I. And this result confirms the above mentioned analogy between the obtained PSDs.

3.1.6. Influence of the carrier gas pressure

Fig. 6 shows the effect of the carrier gas pressure on the median diameter of the obtained PSDs. Other distribution parameters are given in Table II, experiences 18 to 21. It can be observed that the particle size decreases when the carrier gas pressure increases. This effect is produced by the existence of holes in the glass nozzle which gives vapour alkoxide droplets of low size by increasing the pressure difference between the glass nozzle and the hydrolysis chamber. The heat treated particles show the same behaviour as the corresponding as-prepared particles. On the other hand, polydispersity decreases when the carrier gas pressure is increased and the PSDs obtained for high pressures can be considered as monodisperse although their particle size is above 100 nm. These results show that monodisperse PSD of particle diameter below 100 nm can be obtained by using high pressures in the carrier gas stream.

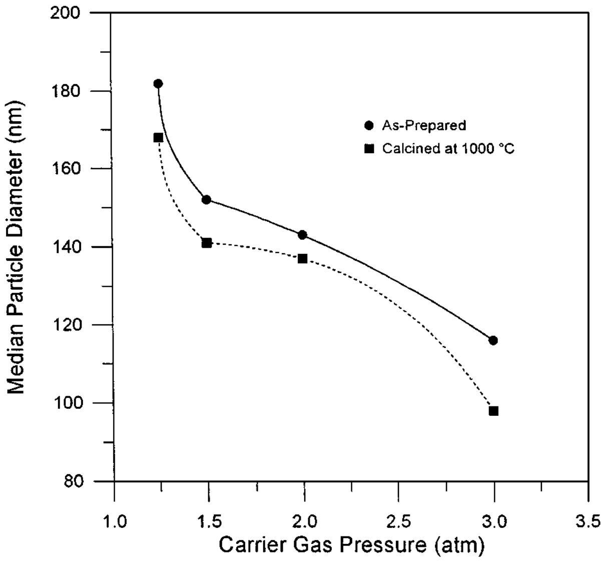


Figure 6 Influence of the carrier gas pressure in the median particle diameter.

3.2. Infrared spectroscopy

Fig. 7 shows the FT-IR spectra of the hydrous titania oxide particles prepared in different experimental

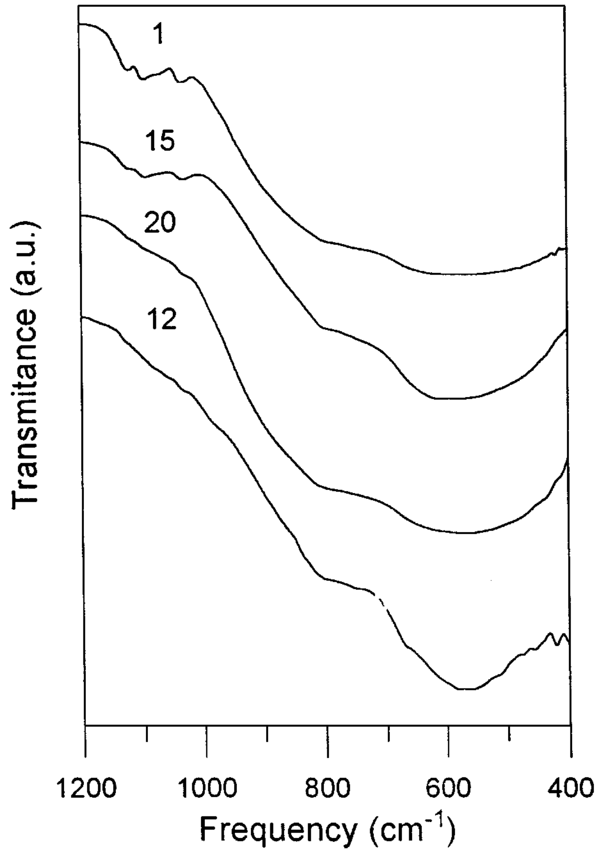


Figure 7 Infrared Spectra of the nanoparticles for different experimental conditions (numbers correspond to experimental conditions given in Table I).

conditions. Numbers above each spectrum corresponds to those given in Table I. This figure only shows the most representative spectra, however a careful analysis was carried out for all of them. In these spectra can be observed a wide band with a maximum about 615 cm^{-1}, which correspond to the Ti-O stretching in Ti-O-Ti and Ti-OH bonds of the hydrous titania oxide, and different low intensity bands around 1200–950 cm^{-1} which corresponds to the presence of *n*-BuOH and/or non-hydrolysed TTB. In the 1200–950 cm^{-1} spectral region the *n*-butanol gives three high intensity bands located at 1074, 1046 and 1030 cm^{-1}, four medium intensity bands lying at 1114, 1012, 992 and 953 cm^{-1}, and a shoulder at 1062 cm^{-1} close to the 1074 cm^{-1} band. On the other hand, for the same spectral region, TTB gives three high intensity bands at 1126, 1100 and 1039 cm^{-1}, and a medium intensity band located at 969 cm^{-1} [14, 15]. The FT-IR spectra of the Fig. 7 show different intensities for the IR bands which appear in the 1200–950 cm^{-1} spectral region. This results corresponds to the presence of *n*-butanol and/or TTB in the obtained titanium hydrous oxide particles. The above mentioned IR bands of *n*-butanol and TTB were used in order to study the degree of hydrolysis of the TTB vapours during the formation of titanium hydrous oxide particles.

FT-IR spectra were subjected to a deconvolution procedure where the above mentioned bands of *n*-BuOH and TTB were assumed to be a gaussian profile. Each band can be defined by three parameters: intensity, half-wide and frequency. Through an iterative process the experimental spectrum can be fitted by the corresponding theoretical gaussian bands. The iteration process is finished when the minimum deviation between experimental and theoretical spectra is achieved. Here, the area of each convoluted gaussian band can be determined through simple integration. Such band area is proportional to the amount of the corresponding chemical bond. Therefore, a semiquantitative information can be obtained by using this deconvolution process [16].

The deconvolution procedure was performed to the FT-IR spectra of the titanium hydrous particles. First of all the *n*-BuOH and TTB spectra were deconvoluted in order to fit them with the minimum error in the band parameters (intensity, half-wide and frequency) of their corresponding IR bands. These bands were used as the starting point for the deconvolution process. Values of the integrated band areas are given in Table III. This table only shows the results of the IR bands of TTB and *n*-BuOH of higher intensity and half-wide. This makes possible to achieve the minimum error in the band area measurement. The analysis of these values gives the following discussed results. The hydrolysis of the TTB increases as the particle size of the titanium hydrous oxide particle decreases. Particles below 100 nm do not show the presence of TTB, and this corresponds to the diffusion of water inside the titanium hydrous oxide particle by means of their specific surface area. Values of specific surface area as high as 180 m^2/g have been found for these particles [12]. The presence of a higher concentration of water vapour in the hydrolysis chamber do not change this result, as it can be seen in experiences 1, 8 and 9 of Table III. When the water bath is set to the higher temperature a lower concentration of non-hydrolysed TTB is observed. This result shows that increasing the water concentration in the hydrolysis chamber the hydrolysis of TTB is also increased. However, it must be observed that the size of the particles is smaller in this case and this smaller particle size may give a higher hydrolysis of the TTB.

TABLE III Integrated FT-IR band areas (a.u.)

Experience number	1130 cm^{-1}	1046 cm^{-1}	*R*
1	0.28	0.13	2.15
2	1.25	0.12	2.08
3	0.14	0.08	1.75
4	0.00	0.00	—
5	1.31	0.13	2.38
6	0.30	0.13	2.50
7	0.28	0.13	2.15
8	0.20	0.10	2.00
9	0.30	0.12	2.50
10	0.24	0.11	2.18
11	—	—	—
12	—	—	—
13	—	—	—
14	—	—	—
15	0.25	0.12	2.08
16	0.08	0.04	2.00
17	0.06	0.04	1.5
18	0.14	0.08	1.75
19	0.12	0.08	1.50
20	0.11	0.07	1.57
21	0.03	0.04	0.75

In experiences where the pressure of the nitrogen carrier gas, system vacuum, flow of the nitrogen-alkoxide stream and dilution with other alcohol is modified it is always observed the same behaviour, i.e. the hydrolysis of TTB increases when the final particle size decreases.

As we said in the experimental section, the raw TTB is mixed with a 1% of *n*-BuOH. This alcohol is also produced during the TTB hydrolysis and can be removed from the titanium hydrous oxide particle by a diffusion process in the hydrolysis chamber and also during the drying step of the obtained particles. The deconvolution procedure has been also used for studying the concentration of *n*-BuOH which remains inside the particles. The results are also given in Table III. These results show the same behaviour as those of non-hydrolysed TTB, and the concentration of *n*-BuOH remaining into the obtained particle decreases when the particle size decreases. In Table III the ratio, *R*, of the IR band areas of TTB and *n*-BuOH is also given which may inform about the hydrolysis of TTB. This ratio is 2.02 for particle sizes above 300 nm, and are below such value for lower particle sizes. These results show that some amount of *n*-BuOH is removed from the obtained particles during the drying step, but some part remains after drying retained in pores. For particle sizes below 300 nm the hydrolysis of TTB is high and the dried particle contains mainly hydrous titanium oxide and *n*-BuOH. However, for particle sizes above 300 nm the *n*-BuOH is removed and the particle contains mainly hydrous titanium oxide and TTB.

4. Conclusions

Spherical hydrous titania oxide particles have been prepared by the vapour-phase hydrolysis method. Titanium tetrabutoxide and deionized water were used as the starting raw materials. Different reaction parameters have been studied in this work, being the titanium alkoxide temperature the most important in order to obtain particles of low particle size. For a temperature of 125 °C particles of mean size below 100 nm are obtained. When the obtained particles are heat treated up to 1000 °C the mean particle size decreases due to the particle shrinkage. The extend of the hydrolysis reaction taking place during formation of the hydrous titania oxide particles has been studied by FT-IR spectroscopy. It has been observed that when the particle size decreases the concentration of the titanium alkoxide retained inside the particle also decreases. Particles of mean size below 300 nm are mainly formed by hydrous titania oxide and adsorbed *n*-butanol, however for particle sizes above 300 nm their composition is hydrous titania oxide and non-hydrolysed titanium alkoxide.

Acknowledgements

This work has been supported by the Spanish Ministerio de Educacion y Ciencia under the CICYT project number MAT96-0564.

References

1. C. J. BRINKER and G. W. SCHERER, "Sol-Gel Science" (Academic Press, Boston, 1990) p. 235.
2. E. MATIJEVIC, "Science of Ceramic Chemical Processing" (John Wiley & Sons, New York, 1986) p. 463.
3. E. MATIJEVIC, *Acc. Chem. Res.* **14** (1981) 22.
4. E. MATIJEVIC, "Ultrastructure Processing of Ceramic, Glasses and Composites" (John Wiley & Sons, New York, 1994) p. 334.
5. T. A. RING, *Mater. Res. Soc. Bull.* **12** (1987) 34.
6. E. A. BARRINGER and H. K. BOWEN, *J. Amer. Ceram. Soc.* **65** (1982) C199–C201.
7. B. FEGLEY, E. A. BARRINGER and H. K. BOWEN, *ibid.* **67** (1984) C113–C115.
8. J. H. JEAN and T. A. RING, *Amer. Ceram. Soc. Bull.* **65** (1986) 1574.
9. H. T. HARRIS and C. H. BYERS, *J. Non-Cryst. Solids* **103** (1988) 49.
10. J. L. LOOK and C. F. ZUKOSKI, *J. Amer. Ceram. Soc.* **75** (1992) 158.
11. H. K. PARK, D. K. KIM and C. H. KIM, *ibid.* **80** (1977) 745.
12. J. RUBIO, J. L OTEO, M. VILLEGAS and P. DURAN, *J. Mater. Sci.* **32** (1997) 643.
13. B. FEGLEY, P. WHITE and H. K. BOWEN, *Amer. Ceram. Soc. Bull.* **64** (1985) 1115.
14. S. DOEUFF, M. HENRY, C. SANCHEZ and J. LIVAGE, *J. Non-Cryst. Solids* **89** (1987) 206.
15. M. J. VELASCO, F. RUBIO, J. RUBIO and J. L. OTEO, *Spectroscopy Letters* **32**(2) (1999).
16. J. RUBIO, F. RUBIO and J. L. OTEO, *J. Mater. Sci.* **26** (1989) 2841.

Received 2 September 1998
and accepted 29 January 1999