On the effects of the sol–gel synthesis parameters on textural and structural characteristics of TiO$_2$

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The effects of alcohol/alkoxide, water/alkoxide molar ratios, acid addition, type of solvent, reaction temperature and calcination temperature on textural, structural and morphological characteristics of TiO$_2$ were studied. The results show that surface area, pore size distribution and crystalline phases were very sensitive to preparation conditions.

Keywords: TiO$_2$ synthesis; sol–gel method; texture and structure of TiO$_2$; TiO$_2$ preparation conditions

1. Introduction

TiO$_2$ has been used as a support in catalysts such as V$_2$O$_5$/TiO$_2$, Mo/TiO$_2$ [1], Pt/TiO$_2$ [2], and Rh/TiO$_2$ [3]. In the last two cases, it has been shown that TiO$_2$ promotes strong metal support interactions (SMSI). TiO$_2$ has traditionally been obtained by TiCl$_4$ hydrolysis in aqueous ammonia solutions. However, the need to control the support characteristics has motivated several research groups to look for new methods of synthesis. One of these methods is the sol–gel [4–6], which has been used to obtain high purity materials. The method basically consists of the hydrolysis of an alkoxide to form a sol, followed by gelling, ageing, drying and thermal stabilization. Each step can be controlled and modified in order to obtain a specific material, with high surface areas, narrow pore size distribution, and narrow particle size distribution.

Considering the unusual texture and structure of the titania, we have prepared this support using the sol–gel method. Here we report the effects of synthesis parameters on properties such as surface area, pore size distribution, crystalline phases and morphology. Parameters under study were alcohol/alkoxide, water/alkoxide molar ratios, acid addition, type of solvent, reaction temperature and calcination temperature.

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2. Experimental

2.1. SYNTHESIS

The general procedure was as follows: a solution of alcohol, water and HNO_3 was prepared and added dropwise to a reactor containing a solution of alcohol and alkoxide under continuous stirring. The solution gelled within 20 min after the water addition had finished, except for the higher dilution samples which took around 2 h. At the gelling point the stirring was stopped, and the gel was aged for 24 h. The residual alcohol was eliminated by distillation. The synthesis conditions for the different samples are shown in table 1.

For the cases in which nitric acid was not used, the same procedure was followed, except that after the water addition had finished the polycondensate obtained was kept under reflux for 12 h.

After the ageing step, the samples were dried at 80°C under vacuum. Calcination was performed under the following program: the sample was heated, under an air flow of 40 ml/min, at a rate of 3°C/min from room temperature to 100°C, kept at this temperature for 30 min, then heated at the same rate to 300°C, kept here for 1 h, and finally the temperature was raised to 500°C and maintained here for 2 h.

2.2. MATERIALS

Ethanol, isopropanol and HNO_3 were obtained from Baker. Titanium (IV) butoxide was from Aldrich. Bidistilled water was used.

2.3. CHARACTERIZATION

DTA and TGA analyses were performed in a Perkin Elmer DTA 1700/TGA-2, under air atmosphere, at a heating rate of 10°C/min. X-ray diffraction patterns were measured and evaluated with a Siemens D500 diffractometer,

Table 1
Synthesis parameters of TiO_2

Sample	Solvent	Temp. (°C)	Molar ratios [a]		
			ROH/OBu	H₂O/OBu	H⁺/OBu
TIP1	isopropanol	25	8.34	8.9	–
TIP2	isopropanol	25	20.0	20.0	0.2
TIP3	isopropanol	75	65.1	20.0	0.2
TIP4	isopropanol	25	65.1	20.0	0.2
TE1	ethanol	75	5.46	8.9	–
TE2	ethanol	60	27.3	8.9	0.2
TE3	ethanol	25	85.26	20.0	0.2

[a] OBu: $Ti(OBu)_4$.

using Cu K$_\alpha$ radiation. Surface areas and pore size distribution were measured by nitrogen adsorption at 75 K on a Micromeritics Accusorb 2100 E equipment. SEM images were obtained on a JEOL 100 CX microscope fitted with STEM attachments and a Tracor 5500 system.

3. Results and discussion

3.1. SYNTHESIS

The preparation of TiO$_2$ via sol–gel is affected by variations in the synthesis conditions. The gel was properly obtained if a catalyst (nitric acid) was used, otherwise an opaque suspension, indicating the formation of the titanium hydroxide, was obtained. It was found that the gelling time increased as the dilution increased (higher alcohol/alkoxide ratio), and the gel formed was transparent and rigid.

During the ageing step the excess alcohol was expulsed from the gel, with a consequent shrinking. In general the shrinking was more pronounced in gels synthesized using ethanol, suggesting the formation of denser and less porous gels.

3.2. THERMAL BEHAVIOUR

Typical thermal gravimetric results are shown in fig. 1. In these TGA curves two main zones were identified. The first zone corresponds to the range 70–200°C which is assigned to the elimination of physically adsorbed water and
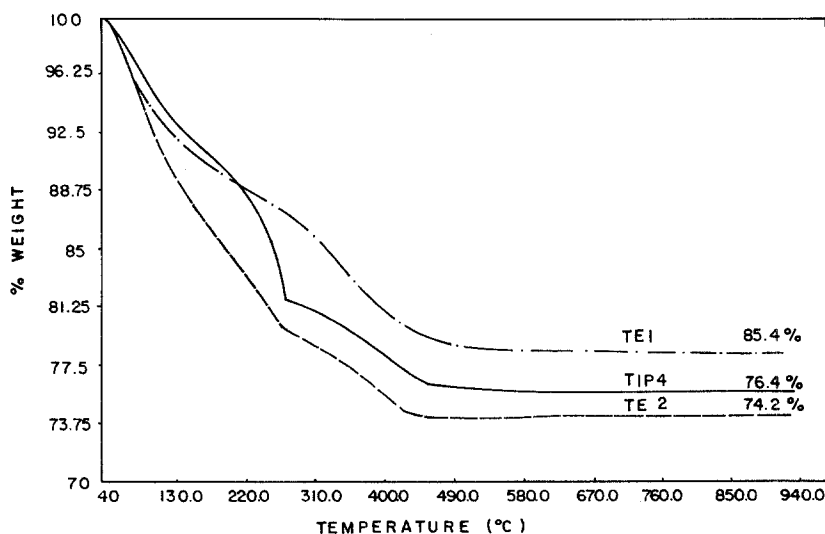
Fig. 1. Thermogravimetric analysis curves of TiO$_2$ synthesized with ethanol (TE1, TE2) and isopropanol (TIP$_4$) as solvents.
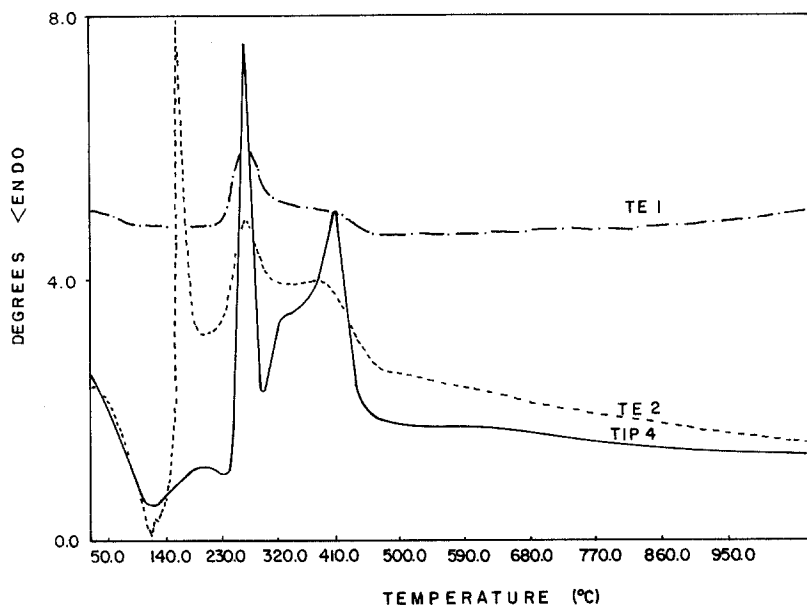
Fig. 2. Differential thermal analysis curves of TiO$_2$ synthesized with ethanol (TE1, TE2) and isopropanol (TIP4) as solvents.

alcohol. The second zone lies between 260 and 460°C and it corresponds to the burning of residual organic material and chemically adsorbed water.

In general weight losses were higher for samples where the gel was effectively obtained. It was also observed that preparations obtained at the higher temperatures (75°C) showed the minimum weight losses.

The differential thermal analysis corresponding to the TGA results shown in fig. 1 are given in fig. 2. The curves have an endothermic peak at 70–200°C, which corresponds to the elimination of physically adsorbed water and alcohol; one exothermic peak at around 240–300°C which is asigned to the elimination and burning of organic material; and another exothermic peak at around 400°C, corresponding to the crystallization of the anatase phase. This last peak was more noticeable for amorphous precursors. For the specific case of sample TE2, a very intense peak was observed at 170°C, which was associated to the elimination and burning of ethanol. At this point the sample blew up. It appears that this particular set of preparation conditions used for this sample: high temperature, low water/alkoxide ratio and relatively low alcohol/alkoxide ratio, induces this behaviour, since this effect was not observed in any of the other samples.

3.3. PHASE STRUCTURE

X-ray diffractograms for the dried samples are shown in fig. 3, whereas those corresponding to the samples calcined at 500°C are given in fig. 4. The spectra
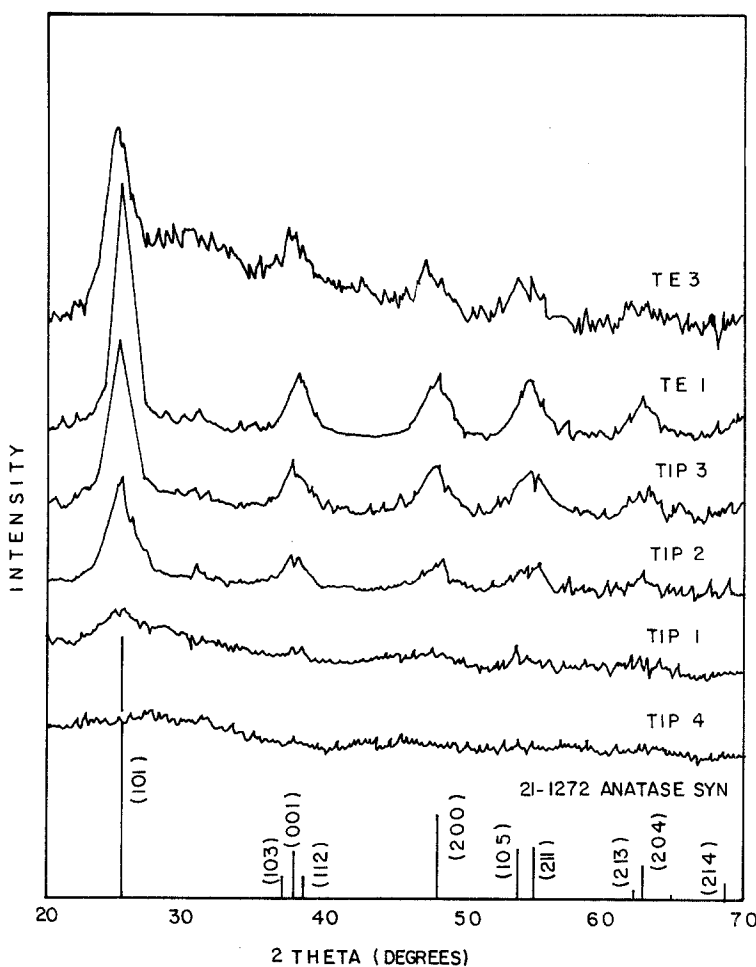
Fig. 3. X-ray diffraction patterns of TiO_2 dried samples (nomenclature as in table 1).

obtained in figs. 3 and 4 are compared with the 21-1272 anatase ASTM card. For the dried samples it is seen that most of the samples show the anatase microcrystalline phase. The exceptions are two samples prepared using iso-propanol as solvent, which were amorphous. These two amorphous samples were synthesized at the following conditions: room temperature, with no acid addition, thus the gel was not formed; and at high dilution (high alcohol / alkoxide ratio) in the case of gel samples. On the other hand, the most crystalline anatase phase was obtained in samples synthesized at the higher temperature (75°C) with and without the acid catalyst addition.

In the case of the calcined samples shown in fig. 4, the phase present is anatase. Only in the case of the sample synthesized with ethanol as solvent, at high dilution and room temperature, a small percentage of rutile was obtained.
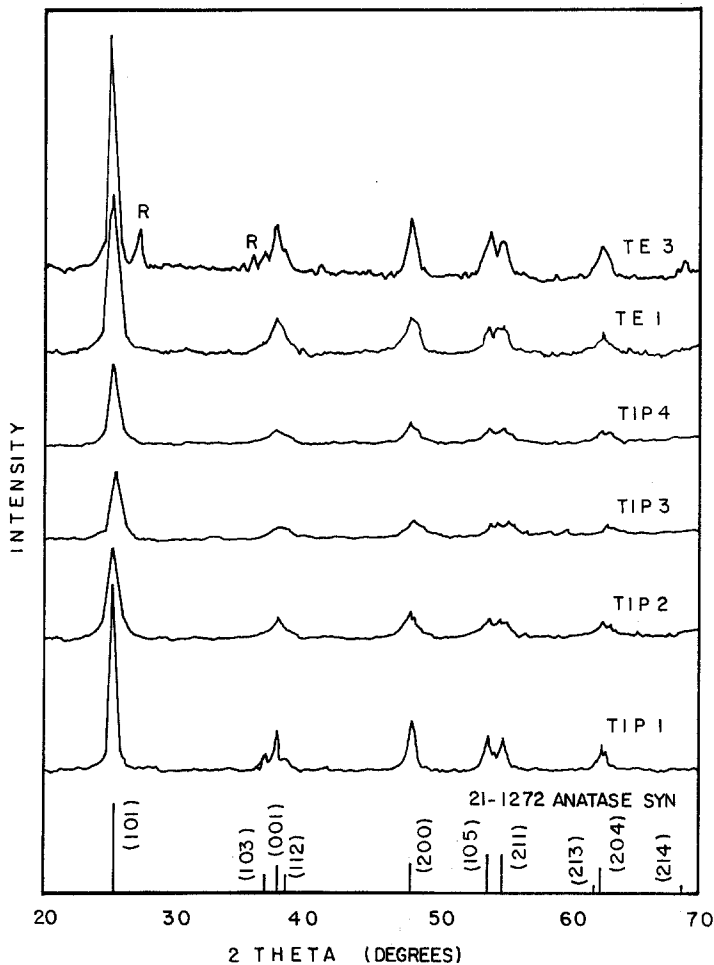
Fig. 4. X-ray diffraction patterns of TiO_2 calcined samples (R: rutile phase).

It was also observed that the most crystalline anatase phase appeared in sample TIP1, which did not form a gel.

3.4. TEXTURAL CHARACTERISTICS

BET surface areas of dried and calcined samples are given in table 2. The surface areas obtained cover a wide range, from 92 to 646 m²/g. Variations in alcohol/alkoxide ratio and synthesis temperature gave different results for samples prepared in isopropanol and ethanol. Solids obtained with isopropanol as solvent gave high surface areas, which decreased as the alcohol/alkoxide ratio increased and as the synthesis temperature increased. However, the solids obtained with ethanol as solvent showed smaller surface areas, and gave the opposite effect as the temperature and alcohol/alkoxide ratio were varied. This

Table 2
Surface area of dried and calcined samples measured with N$_2$ adsorption at 75 K

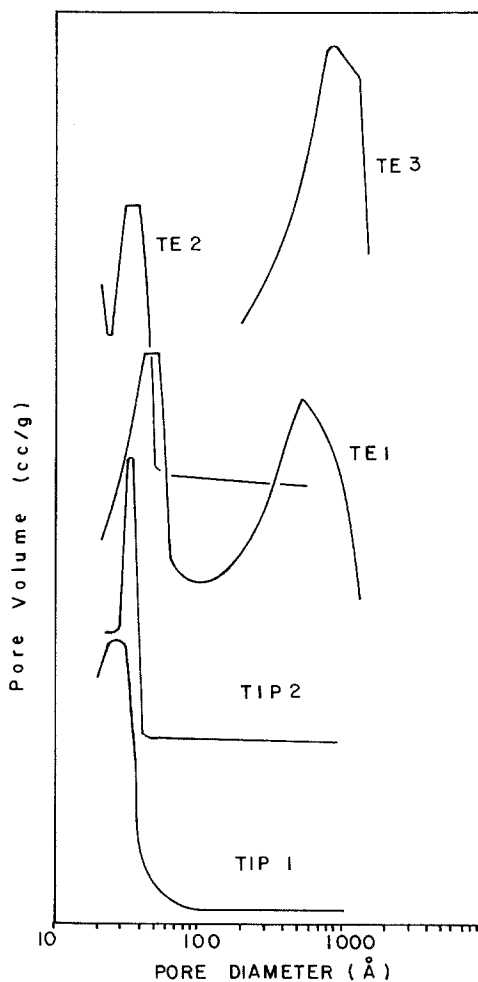| Sample	Surface area (m^2/g)	
	Dried samples (80°C)	Calcined samples (500°C)
TIP1	471	15
TIP2	518	113
TIP3	362	113
TIP4	647	87
TE1	221	106
TE2	209	47
TE3	93	9

Fig. 5. Pore size distribution of TiO$_2$ dried samples (nomenclature as in table 1).

effect might occur due to the exchange of radicals between the alkoxide and the solvent, the difference in size of ethanol and isopropanol, and on the linear or branched type of solvent. The lower surface areas for the samples prepared with ethanol as solvent correlate with the observation that shrinkage of the gels was more pronounced in these samples, as mentioned above.

In thermally treated samples the pore structure collapsed and the surface area decreased. The decrease in surface area is less pronounced in solids synthesized at high temperatures with and without the acid catalyst. The reduction in surface area is accompanied by the formation of a more crystalline phase, as shown by the X-ray results. Sintering and crystallization of the amorphous titania are occurring during calcination.

Pore size distributions of dried samples are shown in fig. 5. Titania prepared with isopropanol as solvent, showed sharp pore size distributions, with main pore size around 30 Å. In the case of the solids prepared with ethanol, the sample obtained without acid showed a bimodal distribution, and that prepared with the highest dilution had only macropores.
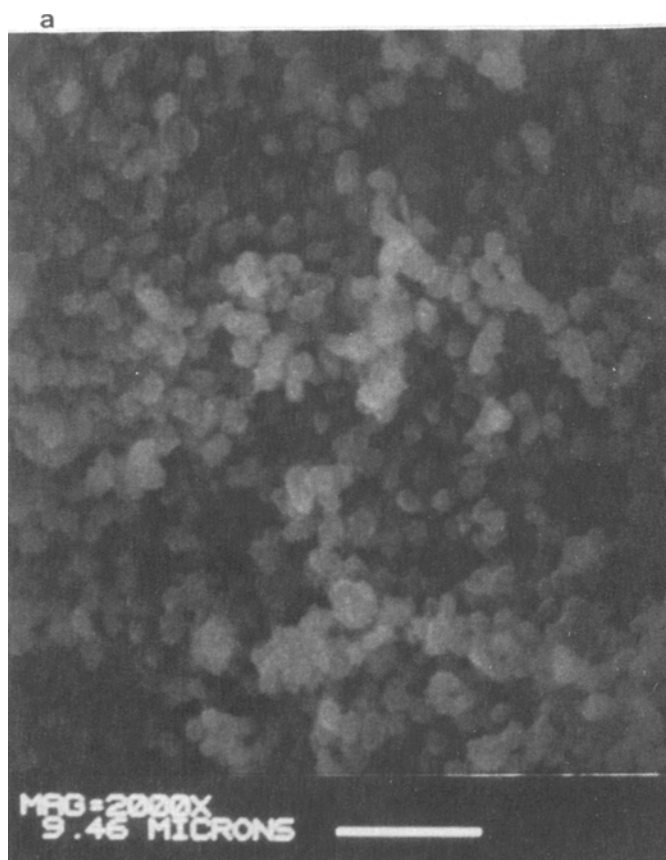

Fig. 6. Scanning micrographs of dried TIP1 (a), dried TE1 (b) and calcined TE2 (c) samples.
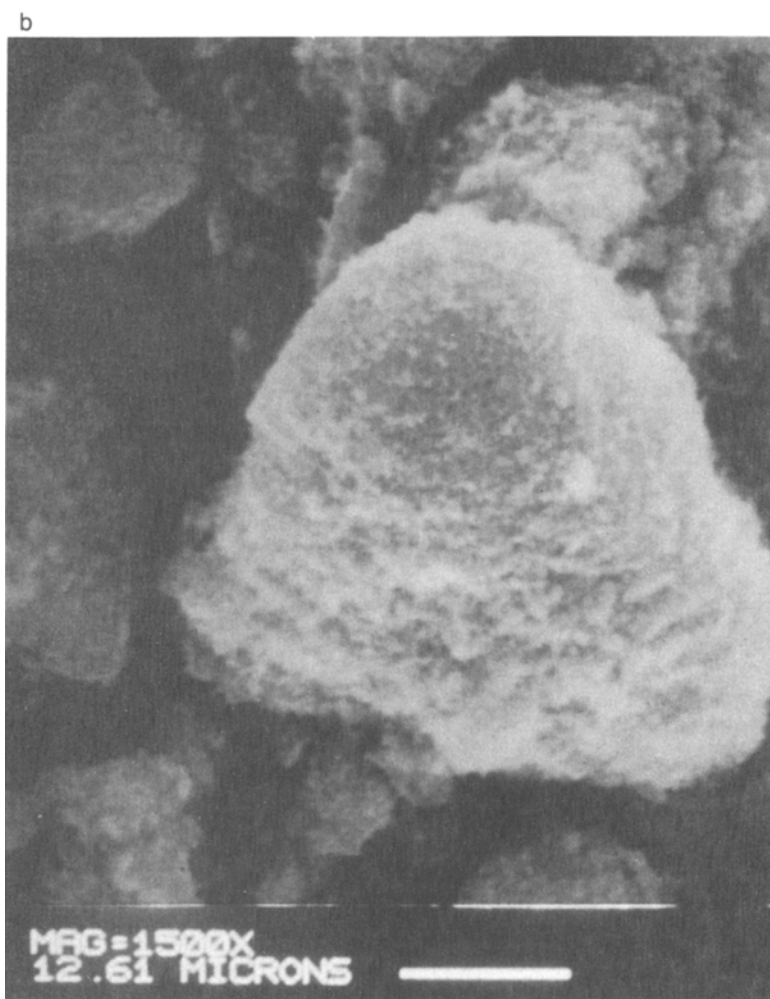
Fig. 6 (continued).

3.5. MORPHOLOGY

The grain morphology and aggregation state of the TiO_2 gels were character-ized by scanning microscopy, as shown in figs. 6 and 7. Those are important parameters that correlate with textural and structural characteristics of the solids. For example, dried TIP1 gels have a very narrow grain size distribution and shape (figs. 6a, 7). These microspheroids form compact aggregates and they are the result of a very homogeneous nucleation during synthesis. In contrast to this, figs. 6b and 6c show uneven grain size and shape obtained with the dried TE1 and calcined TE2 samples (fig. 7), which correspond to samples synthesized with ethanol. The grain size distribution, as illustrated in fig. 7, indicates

c

MAG=300X
63.07 MICRONS

Fig. 6 (continued).

changes when the amorphous-like or microcrystalline gels are calcined at 500°C, as is the case of sample TE2. In the case of the samples shown in this figure the change in the grain size indicates the coalescence of the fine material.

4. Summary

TiO_2 has been prepared by the sol–gel method. Variations in the synthesis conditions produced solids of different characteristics. It was found that param-
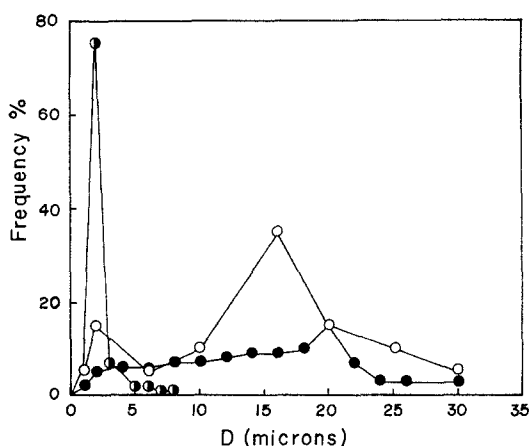
Fig. 7. Grain distribution of TiO$_2$ gels obtained from SEM. (◑) TIP1, (●) TE1, (○) TE2.

eters such as type of solvent, synthesis temperature, acid addition, alcohol/alkoxide and water/alkoxide molar ratios influence the texture, structure and morphology of the samples. The solids obtained exhibited high surface areas, which decreased strongly upon calcination at 500°C. Microcrystalline anatase was obtained after drying at 80°C in most of the samples, except in two cases where isopropanol was used as solvent, one for which nitric acid was not added, and another prepared with nitric acid but at high alcohol/alkoxide molar ratio. Calcination at 500°C of microcrystalline anatase brings about the coalescence of the fine material, producing larger size particles. Amorphous titania crystallizes to anatase after calcination.

References

[1] W. Zhaobin, X. Qin and G. Xiexian, Appl. Catal. 75 (1991) 171.
[2] S.J. Tauster, S.C. Fung and R.L. Garten, J. Am. Chem. Soc. 100 (1978) 9.
[3] S.J. Tauster, S.C. Fung, R.T.K. Beker and J.A. Horsley, Science 22 (1987) 1121.
[4] E.A. Barringer and H.K Bowen, J. Am. Ceram. Soc. 15 (1987) C-199.
[5] M.A. Anderson, M.J. Gieselman and Q. Xu, J. Membrane Sci. 39 (1989) 243.
[6] B.E. Yoldas, J. Mater. Sci. 21 (1986) 1087.