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DSC and FT-IR analysis of the drying process of titanium alkoxide derived precipitates

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Abstract

The drying process of titanium alkoxide-derived precipitates has been studied by means of FT-IR spectroscopy and DSC analysis. From the FT-IR spectrum, it has been possible to observe that unhydrolyzed alkoxide molecules continue the hydrolysis process by using water molecules retained inside the structure of the precipitate or formed by condensation of the Ti–OH groups. However, the quantification of the water content inside the precipitate was carried out by DSC analysis. This technique also allowed to determine two kinds of water molecules: free or interstitial water and coordinatively bound water. These two kinds of water gave two endothermic peaks at ca. 160–180° and 305°C, respectively. The transformation of the amorphous precipitate to a crystalline one is detected by an exothermic peak at ca. 314°C. The elimination of the coordinatively bound water is associated with this crystalline transformation. © 1999 Published by Elsevier Science B.V. All rights reserved.

Keywords: Sol–Gel; Titanium butoxide; Drying; Differential scanning calorimetry; FT-IR spectroscopy

1. Introduction

It is well known that transition metal alkoxides are highly reactive chemical compounds [1]. These compounds react vigorously with water in an alcoholic medium through hydrolysis–condensation reactions to form oxopolymers which grow into an oxide network [2]. By controlling the hydrolysis and condensation reactions, it is possible to obtain a gel or a precipitate which, by carefully controlled drying and sintering processes, lead to a bulk mass or a powder [3]. However, in some cases, the hydrolysis reaction is not complete and un-hydrolysed alkoxide groups remain in the resulting product [4]. This is seen in the case of titanium alkoxides [5,6]. Several studies [7,8] suggest that hydrolysis occurs rapidly whereas the condensation reaction is slow for titanium alkoxides. The slower condensation reaction that succeeds the rapid hydrolysis reaction ultimately results in the precipitation of ‘titania’ particles. The quotes in ‘titania’ are used to indicate that the precipitate is hydrated and also contains unhydrolysed alkoxide groups [9,10]. It is the aim of this work to study the reactions of hydrolysis and condensations that occur in the ‘titania’ precipitate, when it is dried at a low temperature, before the calcination or sintering processes. This work has been carried out by means of differential scanning calorimetry (DSC) and Fourier Transform infrared spectroscopy (FT-IR).

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2. Experimental

Titanium tetrabutoxide (TTB, 99%, Aldrich), *n*-butanol (BuOH, 99%, Aldrich), distilled, deionised water and HNO_3 (Merck, for analysis) were used as starting materials. The molar ratio TTB/BuOH/H_2O was 1/4/4. We have used the parent alcohol, BuOH, in order to avoid alcohol interchange reactions with TTB. Firstly, TTB and BuOH were mixed with a vigorous stirring for 30 min at 25°C and then H_2O (pH 2) was added dropwise for 2 h. It was observed that a white precipitate began to be formed when about one-half of the acid–water solution had been added. The concentration of this precipitate increased during the addition of the water solution. At the end of this process a precipitate, dispersed in the alcohol (BuOH) solution, was obtained.

When the entire acidified H_2O solution was added, the resultant solution, liquid and precipitate mixture, were kept at a constant temperature of 25°C for 7 days while vigorous stirring was maintained. After that, the sample container was opened and the liquid–precipitate mixture was heated at 50°C for 5 days. During this time, stirring was maintained; however, at the end of the day No. 5 most of liquid was removed and the stirrer did not move. At this time, the reaction vessel contained a white precipitate in which no clear liquid was observed. We consider this time as the starting point of the drying process. The 'titania' precipitate, which we call a 'wet precipitate', was then dried in an oven at 50°C for 35 days at room atmosphere and pressure. At the end of this time a 'dried precipitate' was obtained.

This drying (35 days at 50°C) of the 'wet precipitate' was studied by the DSC and FT-IR spectroscopic techniques. DSC experiments were carried out on a Perkin–Elmer DSC-7 equipment at a heating rate of 10°C min^{-1}, in an atmosphere of dried nitrogen. FT-IR spectroscopic experiments were carried out with a Perkin–Elmer FT-IR 1760X spectrophotometer. FT-IR spectra were recorded over the 400–4000 cm^{-1} spectral range using the KBr method. One milligram of the sample was rapidly mixed with 300 mg of KBr and pressed at 8 t for 5 min. A transparent pellet was then obtained. Ten scans, with a resolution of 2 cm^{-1}, were recorded for each resulting spectrum. The corresponding background was subtracted from each spectrum.

3. Results

The overall reaction of titanium alkoxides yielding TiO_2 consists of the hydrolysis of the metal alkoxide and condensation of the disperse phase material. The following general reactions are given:

$$\text{hydrolysis} \quad M(OR)_x + xH_2O \leftrightarrow M(OH)_x + xROH \qquad (1)$$

$$\text{condensation} \quad M(OH)_x \leftrightarrow MO_y(s) + (x-y)H_2O \qquad (2)$$

where M and R represent the metal (Ti in this case) and the alkyl group, respectively, and (s) denotes that the product is a solid. It should be noted that other chemical reactions, such as alcoholysis and/or oxolation may occur [9]:

$$\text{alcoholysis} \quad M-OR + HOR' \leftrightarrow M-OR' + HOR \qquad (3)$$

$$\text{oxolation} \quad M-OR + HO-M \leftrightarrow M-O-M + ROH \qquad (4)$$

As noted in Section 2, we have used the same parent alcohol (BuOH) so as to avoid the alcoholysis reaction.

In accordance with reaction (1), it is seen that 4 mol of H_2O are needed to complete the hydrolysis of the TTB alkoxide. Kallala et al. [11] have shown that, when using TTB with acidified H_2O, the condensation reaction occurs as an oxolation reaction (Eq. (4)), where H^+ ions both, catalyse the hydrolysis and protonate the Ti–OH leaving groups. The protonation of Ti–OH groups inhibits the nucleophilic attack of Ti by Ti–OH and, as a result, hinders the condensation reaction. This results in the presence of unhydrolysed alkoxide groups in the obtained material. In order to remove these unhydrolysed groups, successive steps of washing with H_2O were carried out [12]. Barringer and Bowen [7] have studied the hydrolysis and condensation reactions of titanium tetraethoxide and have given a kinetic equation for such reactions. Winter [13] and Boyd [14] have studied the hydrolysis behaviour of TTB as a function of water-to-butoxide molar ratio and concluded that the fourth butoxy group was difficult to remove and that water was adsorbed on to the precipitate. In another work, we have studied the

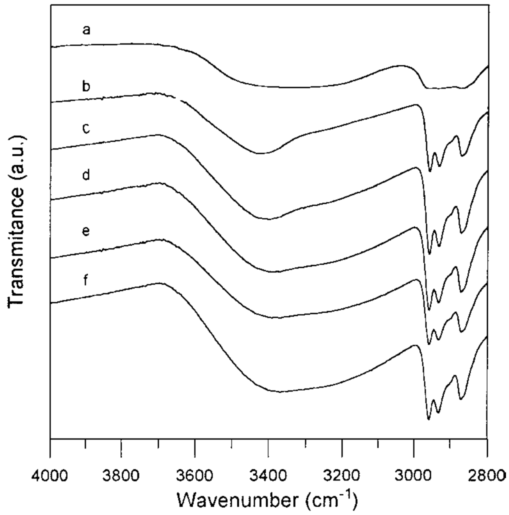

Fig. 1. Infrared spectra of 'titania' precipitates in the spectral range 4000-2800 cm^{-1} at different drying times: (a) 0; (b) 3; (c) 6; (d) 10; (e) 12 and (f) 14 days.

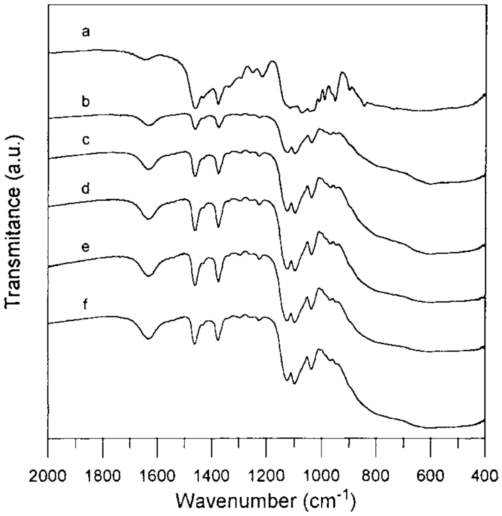

Fig. 2. Infrared spectra of 'titania' precipitates in the spectral range 2000-400 cm^{-1} at different drying times: (a) 0; (b) 3; (c) 6; (d) 10; (e) 12 and (f) 14 days.

hydrolysis of TTB by FT-IR spectroscopy, where we observed that the intensities of the TTB bands decrease ca. 65% in absorbance, probably implying that one unhydrolysed butoxy group remains in the precipitate [15]. The aim of this work is to study the reactions that are taking place in the 'titania' precipitate during the drying step and to follow the evolution of the unhydrolysed alkoxide groups present in such a precipitate. We will show that during drying the hydrolysis of TTB still continues but the fourth butoxy group remains unhydrolysed. For this study, we have used the FT-IR and DSC techniques.

FT-IR spectra in the 2800–4000 and 400–2000 cm^{-1} spectral range of the 'titania' precipitates, dried over different times, are shown in Figs. 1 and 2, respectively. The first spectrum in both the figures (spectrum a) corresponds to time 0 of drying, and Fig. 1 revealed a broad band between 3600 and 3000 cm^{-1}, corresponding to the presence of BuOH and H_2O in the 'titania' precipitate. This broad band corresponds to the O–H stretching vibrations in both, water and alcohol [16]. The presence of BuOH is corroborated by the band located at 1070 cm^{-1} and assigned to C–O stretching in BuOH [16]. The bands situated at 2975, 2930 and 2870 cm^{-1} correspond, respectively, to the C–H stretching of CH_3 and CH_2 groups of BuOH and TTB. The C–H bending vibrations of such groups can be observed in Fig. 2 in the 1300–1500 cm^{-1} spectral region. The O–H bending vibration is observed in Fig. 2 as a weak band close to 1636 cm^{-1}.

In the 800–1200 cm^{-1} spectral region, see Fig. 2, the different bands can be assigned to both, BuOH and TTB. The BuOH molecule gives a high-intensity band at 1073 cm^{-1}, six medium-intensity bands at 1114, 1046, 1011, 992, 953 and 847 cm^{-1}, and a shoulder at 1061 cm^{-1} [16]. On the other hand, the TTB molecule gives three high-intensity bands at 1127, 1084 and 1035 cm^{-1}, a shoulder at 1095 cm^{-1}, and three medium-intensity bands at 994, 969 and 901 cm^{-1} [6,15]. Below 800 cm^{-1}, the broad band due to the envelope of the phonon bands of a Ti–O–Ti bond of a titanium oxide network appears [17]. The absence of any band in this spectral region which could be assigned to the crystalline structures (anatase and/or rutile) of TiO_2 shows that the precipitate is amorphous [18].

Spectra b–f of Figs. 1 and 2 correspond to different drying times. Several features are present in these spectra. Firstly, it can be observed that there is a decrease in the intensity of the broad band between 3000–3600 cm^{-1}, and it is now better defined. In the spectral region 1000–1200 cm^{-1}, there are three well-defined bands located at 1127, 1084 and 1035 cm^{-1}, which correspond to TTB as above. At the same time,

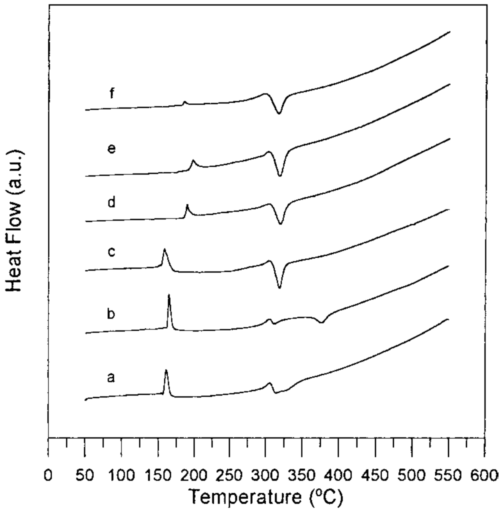

Fig. 3. DSC measured curves for 'titania' precipitates at different drying times: (a) 0; (b) 3; (c) 6; (d) 10; (e) 12; and (f) 14 days.

the broad band due to Ti–O–Ti bonds is also observed, and the C–H stretching (below 3000 cm^{-1}), C–H bending (1360–1470 cm^{-1}) and O–H bending (1636 cm^{-1}) are also well-defined. All of these bands appear during the entire drying time, indicating that H_2O and TTB are present in the 'titania' precipitate.

Different DSC thermograms corresponding to the drying of 'titania' precipitates are shown in Fig. 3. Different exothermic and endothermic peaks are observed. In the DSC thermogram corresponding to the first day of drying (Fig. 3(a)), there appear two endothermic peaks at 161 and 305°C, respectively, and one exothermic peak at 314°C. This exothermic peak appears in all the DSC thermograms and its intensity seems to increase with the drying time. On the other hand, the intensity of the endothermic peak at 161°C decreases and moves to 181°C, and, at the same time, a new endothermic peak appears at 190°C. The exothermic peak is well-characterised in different works [19] and corresponds to the crystallisation of anatase from the amorphous structure of the 'titania' precipitate. Ragai and Lotfi [20] have shown that the temperature at which the amorphous precipitate transforms to anatase is governed by two parameters: the presence of water in the inner coordination sphere of titanium and the presence of chloride ions. In our study, chloride ions do not exist, but the presence of TTB – and possibly BuOH – must be taken into account. However, such transformation always occurs at the same temperature and, therefore, it must depend mainly on the presence of water. The evaporation of water from the 'titania' precipitate must be responsible for all the endothermic peaks which appear in the DSC thermograms. Ragai [21] has shown the existence of three kinds of 'water' on 'titania' precipitates which give three endothermic peaks at ca. 94–107°, 280° and 350–500°C, respectively. These peaks correspond to free or interstitial water, coordinatively bound water and rigidly bound water in the form of hydroxyls ions, respectively. In our study, we must also take into account the possible presence of BuOH in the precipitate, which also gives an endothermic peak due to evaporation during DSC measurement.

In order to make a more exhaustive study of the drying process of 'titania' precipitates using FT-IR spectroscopy and DSC measurements, we have carried out a semi-quantitative and quantitative analysis of FT-IR and DSC results.

4. Discussion

FT-IR spectra were deconvoluted in the corresponding isolated IR bands by assuming they have a Gaussian profile. The deconvolution procedure was carried out as follows: the spectra of H_2O, BuOH and TTB were deconvoluted by using those bands which are described in the literature [6,15–17]. Following that, all experimental 'titania' spectra were deconvoluted by using all of those bands previously found for H_2O, BuOH and TTB where intensity ratios, half-width and position (wave number) of each band were also maintained. Intensities of all of these bands were then changed in order to obtain the best fit between experimental and deconvoluted spectra. Finally, the integrated areas of such bands were computed by normal integration. Integrated areas are related to the concentration of the corresponding chemical bond which gives such IR band and, therefore, a semi-quantitative study can be carried out. Experimental errors between the deconvoluted and measured spectra were always <1%. Fig. 4 shows a typical deconvolution of an FT-IR spectrum. We have carried out the deconvolution procedure in two spectral regions: the first, in the 2800–3700 cm^{-1} spectral range, where O–H stretching vibrations of water and BuOH appear, and the

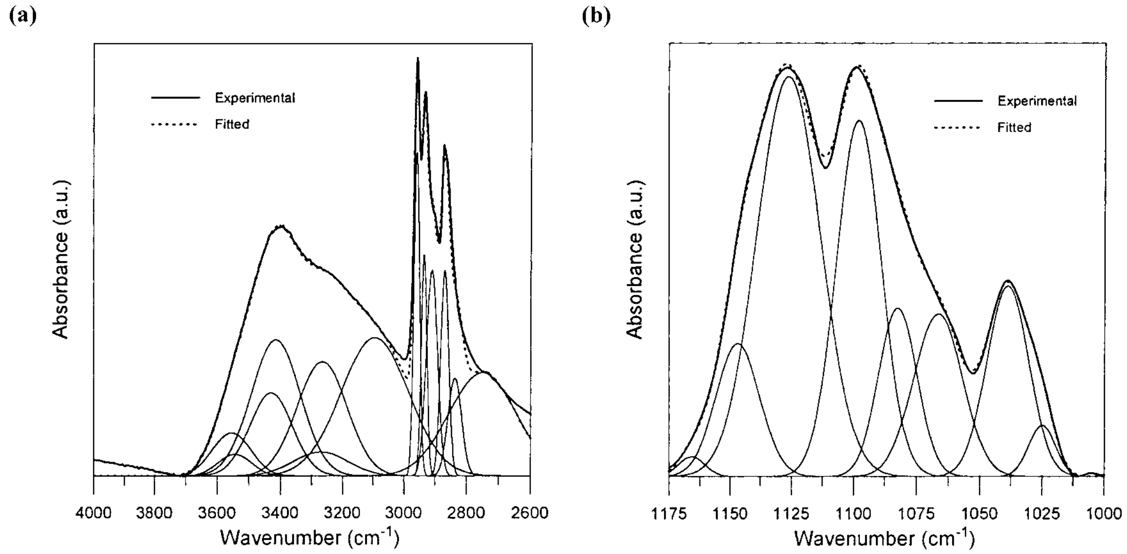

Fig. 4. (a) Deconvolution example of the IR spectrum corresponding to the drying time of 6 days of the 'titania' precipitate in the spectral region 4000-2600 cm^{-1}. (b) Deconvolution example of the IR spectrum corresponding to the drying time of 6 days of the 'titania' precipitate in the spectral region 1175-1000 cm^{-1}.

second in the 950–1200 cm^{-1} range, where C–O–Ti of TTB and C–O stretching vibrations of BuOH take place.

Fig. 5 shows the evolution of the deconvoluted IR bands found at 1125, 1089 and 1037 cm^{-1}, which correspond to TTB and BuOH as we have mentioned above. Some special conclusions can be obtained from this figure: firstly, it is observed that a high concentration of BuOH remains inside the 'titania' precipitate when the drying process begins and this BuOH is removed during the first three days of drying; secondly, TTB is present in the 'titania' precipitate in accordance with the results given by other works [4–8,15] and such unhydrolysed TTB decreases during drying, thus showing that the hydrolysis process of TTB also continues during the drying process [5]. In order to continue the hydrolysis of TTB during drying, the presence of water in the precipitate is necessary. This is confirmed in Fig. 6, which shows the evolution of the IR deconvoluted bands located at 3545, 3415, 3266 and 3090 cm^{-1}. These bands are in the hydroxyl stretching region and should correspond to O–H vibrations of the Ti–OH groups and H_2O molecules. The 3545 cm^{-1} band must correspond to O–H vibrations of the Ti–OH groups and, as it can be observed, these groups increase their concentration during the first 25 days of drying, and thereafter they decrease slowly. This result is associated with the hydrolysis of unhydrolysed TTB molecules and the elimination of water during drying. The observed decrease corresponds to the condensation reaction (Eq. (2)) between

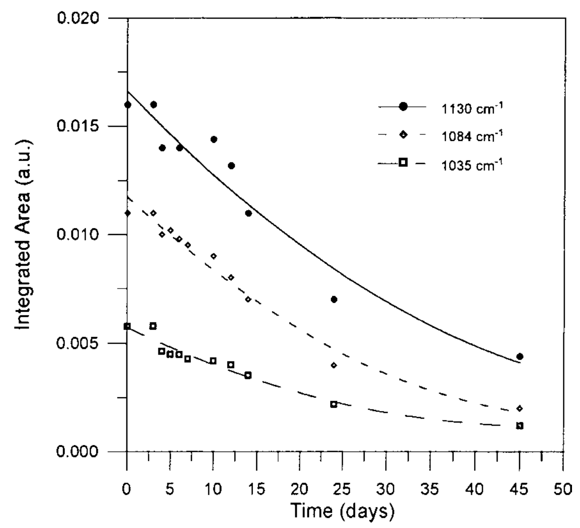

Fig. 5. Time evolution of the integrated areas for 1125, 1089 and 1035 cm^{-1} bands as a function of drying time of the 'titania' precipitate.

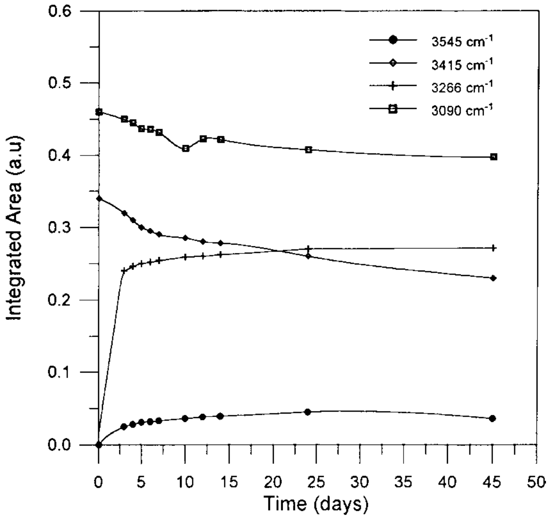

Fig. 6. Time evolution of the integrated areas for 3545, 3415, 3266 and 3090 cm^{-1} bands as a function of drying time of the ‘titania’ precipitate.

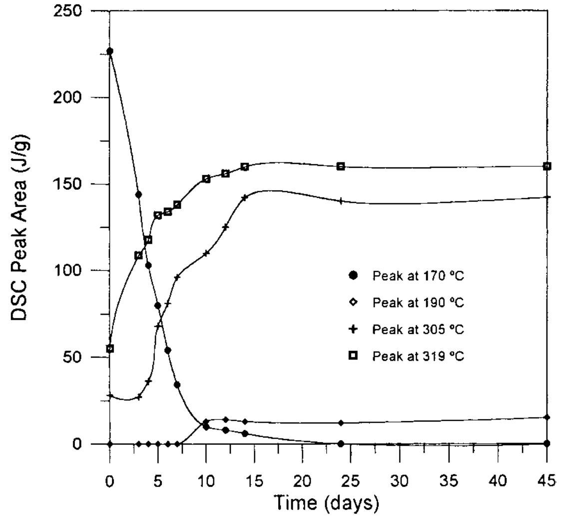

Fig. 7. Variation of the DSC peak area as a function of drying time of the ‘titania’ precipitate.

Ti–OH groups. The other three bands must then correspond to the O–H vibrations of different kinds of H_2O molecules: adsorbed on both the Ti–OH groups and on micropores. The observed decrease for the 3415 and 3090 cm^{-1} bands is mainly due to three effects: consumption of H_2O in accordance with Eq. (1), evaporation of H_2O during drying and elimination of H_2O during the preparation of the IR pellet [22]. The increase of the 3266 cm^{-1} band must correspond to very strongly retained H_2O. As we have shown in another work [22], FT-IR spectroscopy is not an useful technique for studying the drying process of silica gels. However, in the case of titanium alkoxide-derived precipitates, this technique can inform about the presence of H_2O in the precipitate to be able to hydrolyse the remaining unhydrolysed alkoxide groups.

The DSC technique is a more powerful technique in order to study the drying process of alkoxide-derived materials [21]. Results obtained by DSC can be quantified and they are related to the concentration of materials present in the studied sample. Fig. 7 shows the evolution of the peak areas corresponding to the DSC thermograms presented in Fig. 3. As can be observed in Fig. 7, the peak located at ca. 160°C decreases in intensity and disappears after 24 days of drying. This peak corresponds to free or interstitial water in accordance with Ragai [21]. On the other hand, the peak that appears at ca. 190°C increases its intensity within then 7–10 days of drying and after that remains constant. This peak must also correspond to a kind of H_2O more strongly retained in the ‘titania’ precipitate, and it may also be due to the presence of BuOH produced by the hydrolysis of TTB during drying. The high temperature at which it appears must correspond to a more closed structure of the ‘titania’ precipitate as a result of drying.

The endothermic peak appearing at 305°C increases in intensity during the first 10–12 days of drying and is associated to coordinatively bound water, in accordance with Ragai [21]. The behaviour of this peak is similar to that of the exothermic peak that appears at 319°C which is produced by the amorphous-to-crystalline (anatase) transformation. In accordance with this result, it must be concluded that the amorphous-to-crystalline transformation depends on the presence of coordinatively bound H_2O and such transformation occurs if the coordinatively bound H_2O has been removed. Yoldas [23] has shown that the weight loss of ‘titania’ gels is almost complete at ca. 300°C and this result also confirms that the highest temperature of the DSC peaks found in our work is 305°C.

5. Conclusions

This study has shown that a semi-quantitative analysis can be carried out on the drying process of titanium alkoxide-derived precipitates. By using FT-IR and DSC techniques, the evolution of unhydrolysed alkoxide molecules, water and *n*-butanol can be followed. The three IR bands of unhydrolysed titanium alkoxide which are observed at 1125, 1089 and 1037 cm^{-1} show a continuous decrease in intensity with drying time, thus leading to the conclusion that the hydrolysis process still continues during drying.

Two kinds of water molecules have been detected by DSC analysis. One corresponds to the free or interstitial water which gives an endothermic peak at ca. 160°C, and the other kind of water corresponds to coordinatively bound water which gives an endothermic peak at 305°C. The concentration of free water decreases with drying time as a result of evaporation from the precipitate or by reaction with unhydrolysed alkoxide molecules. On the other hand, the concentration of coordinatively bound water increases with the drying time and is associated with the crystalline transformation of the titania precipitate.

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