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THERMOANALYTICAL STUDY OF ACETYLACETONATE-MODIFIED TITANIUM(IV) ISOPROPOXIDE AS A PRECURSOR FOR TiO_2 FILMS

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Thermal decomposition of dried TiO_2 gel, obtained by hydrolysing acetylacetonate-modified titanium(IV) isopropoxide, was monitored by simultaneous TG/DTA/EGA-FTIR measurements in dynamic air up to 900ºC. XRD and FTIR were employed to identify the solid reaction products. Thermal degradation of the TiO_2 gel consists of five distinct mass loss steps, the total mass loss being 43.8%. EGA by FTIR revealed the release of H_2O below 120ºC; followed by acetone, isopropyl acetate and 1-propanol around 200–300ºC, and finally CO and CO_2 up to 550ºC. Highly exothermic reaction at 410-550ºC is caused by the combustion of carbon residues. Crystalline TiO_2-anatase is formed around 500ºC and TiO_2-rutile close to 800ºC.

Keywords: *DTA, EGA-FTIR, sol–gel, TG, titania, titanium complex*

Introduction

The sol–gel processing offers attractive routes to prepare flat and porous TiO_2 films for dielectric, photocatalytic and solar cell applications [1, 2]. Ti-alkoxides are well-known precursors for titania in spite of their being easily hydrolyzed, making their sol–gel transformation very fast and thus difficult to control. The chemical modification of metal alkoxides with alcohols, chlorides, acids or bases, and chelating ligands is commonly used to retard the hydrolysis and condensation rates [3–5]. Acetylacetone (acacH), acting as a bidentate monocharged acetylacetonate ligand (acac), has been used as a stabilizing reagent for titanium tetra-isopropoxide (TTIP) by several authors to prepare TiO_2 thin films [6–9]. Furthermore, it was shown in our recent studies that TiO_2-anatase films prepared by the sol–gel method, using TTIP stabilized by acacH, can yield materials with optical and dielectric properties similar to those obtained with titania, fabricated in more sophisticated and costly facilities [6, 7].

A better understanding of the thermal behaviour of gels formed in a sol–gel process would enable to optimize the calcination conditions and thus improve the properties of TiO_2 films. Recently, Campostrini *et al*. have published pyrolysis studies of hydrolysed TTIP, modified by various stabilizers such as formic [10], oxalic [11] or acetic acid [12] and also, for comparison, without a chelating agent [13]. Studies on the thermal behaviour of commercially available TiO_2 sols have been performed as well [14].

In the present work, the thermal degradation process of hydrolyzed acac-stabilized TTIP was monitored by coupled TG/DTA and TG/EGA-FTIR techniques [15] in dynamic air in the temperature range of 20–900ºC. The aim of the study was to gain a better understanding of the formation mechanism of TiO_2 thin films prepared in this precursor system.

Experimental

Chemicals

Reagent grade chemicals, viz. titanium tetra-isopropoxide (TTIP) and acetylacetone (acacH) from Merck (Darmstadt, Germany) and 2-methoxy-ethanol (2-MOE) from Fluka (Steinheim, Germany) were employed for the syntheses. All chemicals were used as received without any purification.

Synthesis of samples

The stabilizer acacH was slowly added to TTIP in a molar ratio of 1:1 and stirred at room temperature for 30 min. The stabilized TTIP solution was thereafter mixed with 2-MOE in the TTIP:2-MOE molar ratio of 1:10. The solution was refluxed at 130°C for 2 h. The final solution was cooled down to room temperature and filtered through 0.2 μm syringe filter. The solu-

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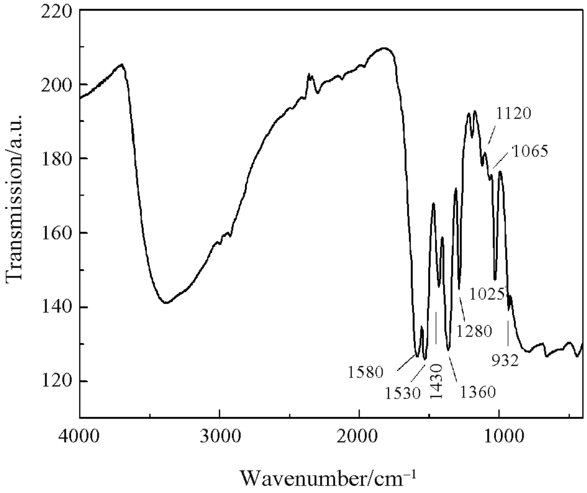

Fig. 1 FTIR spectrum of TiO_2-acac (= hydrolyzed TTIP stabilized by acac) gel at room temperature

tion was held in closed glass bottles and was found to be stable for at least one year. To obtain the gel, the solution was allowed to slowly evaporate under ambient conditions. The solution turned into the gel in a couple of days and a week later a dry gel powder was formed. The dried gel powder, used as a precursor for thermal analysis, is labelled as TiO_2-acac.

Characterization of the precursor, intermediates and final products of its thermal decomposition

FTIR and powder diffraction were used ex situ to characterize the TiO_2-acac precursor, its intermediates and final products of its thermal decomposition. IR spectra of the powdered samples were recorded in the region of 4000–400 cm^{-1} in a Perkin Elmer GX1 spectrometer using the KBr pellet technique. The X-ray diffraction (XRD) patterns were recorded in a Bruker AXS D5005 diffractometer with monochromatic CuKα radiation. The crystalline phases were identified using the JCPDS files. TiO_2-acac and its thermal decomposition intermediates were analysed for carbon content on an Elemental Analysesysteme Gmbh Vario EL CHNOS Elemental Analyser. In addition, the gel was characterized by mass spectrometry using sample introduction by electro-spray.

Thermal analysis

For the simultaneous TG/DTA/DTG studies of TiO_2-acac**,** a Setaram Labsys 2000 instrument was employed. Sample mass of 14 mg was chosen for the experiments performed at the heating rate of 5ºC min^{-1} The measurements were carried out in a dynamic air atmosphere using the gas flow rate of 50 mL min^{-1}. In addition, heat treatments of TiO_2-acac were performed in a preparative scale in air using a Nabertherm laboratory oven. Heat treatment temperatures were determined on the basis of the dynamic TG runs.

TG/DTA, coupled with evolved gas analysis (EGA), was carried out with the Setaram LabSys 2000 instrument using heating rate of 5ºC min^{-1} and air flow rate of 60 mL min^{-1}, open Pt crucibles and a sample mass of 39 mg. The components of evolved gaseous mixtures were identified and monitored using FTIR gas analyser (Interspectrum). The Ranger-AlP Gas cell S/N 23790 (Reflex Analytical Co.) with 8.8 meters path length was maintained at 150°C. The absorption spectra were recorded in the region of 4000–600 cm^{-1} with a resolution of 4 cm^{-1}. Four or two scans were made for spectra. The evolved gases were identified on the basis of their FTIR reference spectra available on world wide web in the public domain spectral library of NIST [16]. The evolution profiles of gases as derivatives of the peak intensity (dI/dt)

Table 1 Decomposition steps, mass losses, temperatures of DTA and DTG peaks as recorded for TiO_2-acac on Labsys 2000 instrument

Experimental details	Step	Temperature range/ºC	DTG max temp./ºC	DTA peak temp./ºC	Mass loss/%	Total mass loss/%
	1	20–120	74	74 endo	8.2	
Heating rate 5ºC min^{-1}	2	120–270	232	250 exo	11.1	
m_0=14.0 mg	3	270–410	330	330 exo	12.9	43.8
	4	410–550	480	480 exo	9.1	
	5	550–900	763	765 exo	2.5	
Pre-heated precursor	1	20–150	80	80 endo*	1.7	
Heating rate 5ºC min^{-1}	2	150–270	240	255 exo	9.8	
m_0=39.0 mg	3	270–410	334	338 exo	17.8	40.9
	4	410–550	484	487 exo	11.6	

*weak

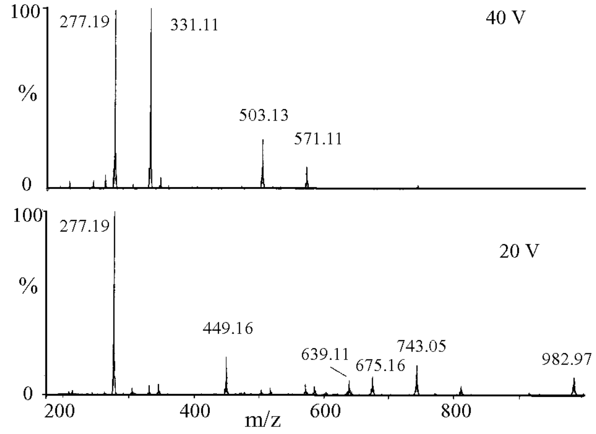

Fig. 2 Mass spectra of TiO_2-acac prepared by electrospraying the precursor sol (TTIP:acacH:2MOE=1:1:10) at 20 and 40 V

or the peak area (d*S*/d*t*), integrated above the baseline, were applied to characterize the evolution dynamics.

Results and discussion

Characterization of the precursor TiO_2-acac

Hydrolysed TiO_2-acac gel is amorphous according to XRD. The IR spectrum of TiO_2-acac gel is presented in Fig. 1. A broad IR band at 3000–3600 cm^{-1} belongs to the hydroxyl group confirming the hydrolysis of TTIP. The peaks around 2950 cm^{-1} correspond to C–H elongation vibrations. The shoulder located at 1600 cm^{-1} could belong to the bending vibration of H_2O. The peaks located at 1580, 1530, 1430 and 1025 cm^{-1} are characteristic for conjugated C–O vibrations [C=C–(C=O) and C=C–(C–)O–] of the acac ligand, bound to a transition metal [17]. The vibrations at 1360 cm^{-1} and 932 cm^{-1} (Fig. 1) could belong to CH_3 umbrella and CH_3–C–CH_3 stretching modes of the isopropoxy group, respectively [18]. The vibrations at 1280, 1120 and 1065 cm^{-1} (Fig. 1), could be also assigned to the isopropoxy group [11].

The mass spectra of the TiO_2-acac precursor, prepared by electrospraying the precursor sol (TTIP:acacH:2MOE=1:1:10), show the profile of the peaks characteristic for the titanium complexes (Fig. 2). The difference in *m/z* between the main peak and the first satellite is one for all the peaks observed, indicating the presence of monocations. At 20 V the major peak of TiO_2-acac is observed at *m/z*=277.19. At higher energy of 40 V, this peak still is the most dominant one together with a new one at *m/z*=331.11. Many of the relatively weak peaks appearing in the range *m/z*=350–982 are no longer present at 40 V and thus the fragmentation pattern is almost completely different.

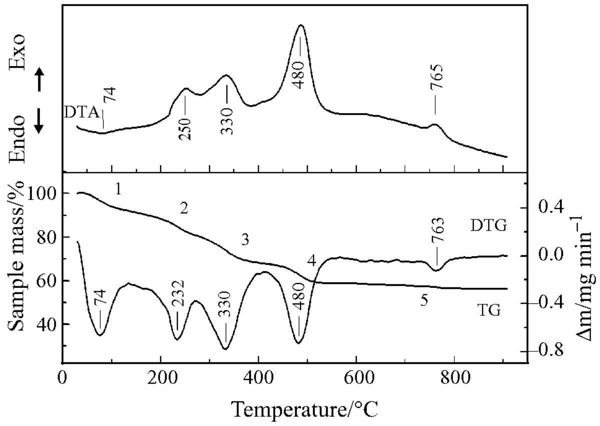

Fig. 3 TG, DTA and DTG curves of TiO_2-acac recorded in flowing air of 50 mL min^{-1} at the heating rate of 5° min^{-1}. The sample mass is 14.0 mg

Thermal analysis

Thermal behaviour of TiO_2-acac was studied in synthetic air up to 900°C. Five mass loss steps could be detected according to the DTG curve at the heating rate of 5ºC min^{-1} (Fig. 3). The first decomposition step of TiO_2-acac in the interval of 20–120°C is a weak endothermic reaction with the mass loss of 8.2% (Fig. 3, Table 1). This step could be assigned to the evolution of water as confirmed by EGA-FTIR (see the EGA section). The following mass loss steps (2, 3, 4) having the DTG maxima at 232, 330 and 480ºC, respectively, are exothermic reactions according to DTA (Fig. 3). A considerable amount of heat evolves around 500ºC. The last small mass loss step above 760ºC is also an exothermic reaction, obviously corresponding to the crystallization of the rutile phase [19]. The total mass loss in the TG curve is 43.8%. The final decomposition product above 800°C is TiO_2 (rutile) as confirmed by

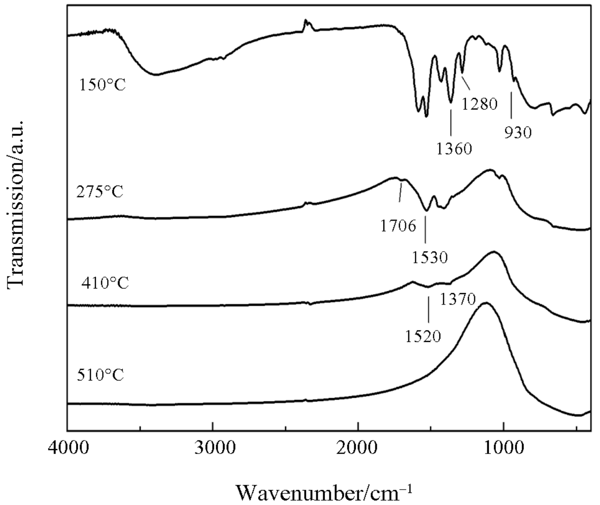

Fig. 4 FTIR spectra of solid intermediates prepared at 150, 275, 410 and 510ºC

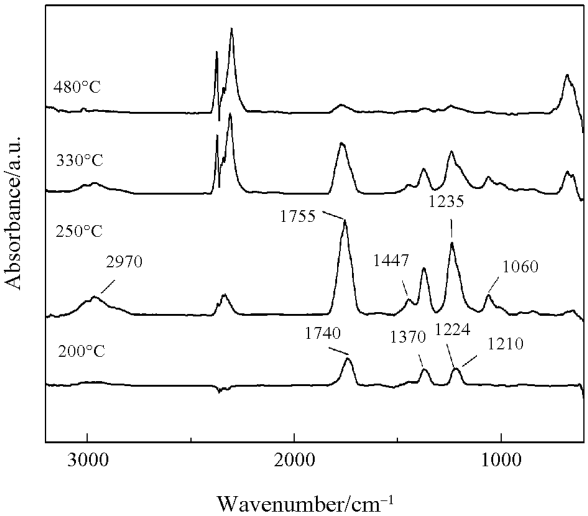

Fig. 5 FTIR spectra of the mixture of gaseous species evolved at 200, 250, 330 and 480ºC

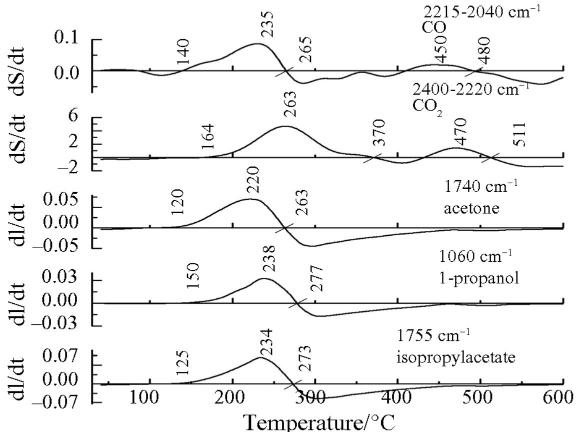

Fig. 6 The evolution profiles of gases

XRD (Table 2). This temperature (800°C) is the same as found by Suresh *et al.* for anatase–rutile phase transformation using acetic acid modified gel precursor prepared at pH 6 [20]. However, depending on the ligands and additives in the system, the transformation temperature may be different [21, 22].

TiO_2-acac heated up to 120ºC was used as a precursor for the coupled TG-EGA analysis. Above 150ºC, the TG/DTA/DTG curves of the preheated TiO_2-acac are strikingly similar to those presented in Fig. 3. The only difference is a significantly lower mass loss of 1.7% in the first step, resulting in the total mass loss of 40.9% (Table 1).

Characterization of the solid decomposition products of TiO_2-acac

According to XRD, the crystalline anatase phase is the decomposition product of the step 4 close to 500ºC. The solid intermediates at lower temperatures are all amorphous. As noted earlier, rutile is the final product at 900ºC. According to elemental analysis, the carbon content increases when going from room temperature up to 150ºC (Table 2). Further annealing decreases the carbon content and around 500ºC carbon is present only in trace amounts.

IR spectra of a TiO_2-acac sample heated up to 150ºC are presented in Fig. 4. The only difference, compared to the precursor, is the weakening in intensity of a broad absorption band in the region of 3600–3200 cm^{-1}, characteristic to water and hydroxyl groups. There are no changes in the position and intensity of the main absorption peaks, however. The observed behaviour corresponds to the first mass loss step of TiO_2-acac, mainly corresponding to the evolution of water. The product of the decomposition step 2 (at 275ºC) shows a significantly changed FTIR spectrum (Fig. 4). The absorptions around 3400 cm^{-1} are weakened in intensity, indicating a reduced content of OH groups in the sample. The vibrations at 1360, 1280, 1200–1100 and 930 cm^{-1}, characteristic to Ti-isopropoxide structure, are vanished. The disap-

Table 2 Gaseous species evolved and composition of solid decomposition products of TiO_2-acac in the temperature interval of 20–900ºC

Step	Temp. range/ºC	Type of the main reaction	Evolved gases	Solid product of the step	
				C/%	Phase by XRD
1	20–120	endo	H_2O	21.8	Amorph.
2	120–270	exo	CH_3COCH_3 $CH_3CH_2CH_2OH$ $CH_3COOCH(CH_3)_2$ CO, CO_2	15.4	Amorph.
3	270–410	exo	CH_3COCH_3 $CH_3CH_2CH_2OH$ $CH_3COOCH(CH_3)_2$ CO, CO_2	10.0	Amorph.
4	410–550	exo	CO_2, CO	<0.1	Anatase
5	550–900	exo	(CO, CO_2)	0	Rutile

pearance of the isopropoxy group in the solid state structure is the most significant feature of the step 2. The vibrations at 1590–1530 cm^{-1} and the absorption at 1706 cm^{-1}, characteristic to C=O bonding [18], are still present in the sample, however.

The decomposition product of the step 3 at 410°C shows only very weak absorptions at 1520 and 1370 cm^{-1}, indicating that only a low number of IR active groups is present in the material. Highly exothermic reaction with a mass loss of ~ 9% in the decomposition step 4 (Fig. 3, Table 1), obviously corresponds to the combustion of elemental carbon (10% at 410°C). IR spectrum of the sample prepared at 510°C shows a broad absorption in the region of 1000–400 cm^{-1} (Fig. 4), characteristic to a Ti-O-Ti network [23].

Evolved gas analysis

The first mass loss step of TiO_2-acac at 20–120°C corresponds to the evolution of water, confirmed by strong characteristic absorptions of H_2O in the IR spectra of evolved gases (not presented here). To avoid the overshadowing of the vibrations of evolved gases and water at higher temperatures, the precursor was pre-heated at 120ºC. Pre-heated TiO_2-acac was then used as a precursor for the TG-EGA analysis with a heating rate of 5ºC min^{-1}. FTIR spectra of the gaseous species evolved at temperatures above 200°C are presented in Fig. 5.

In the temperature range of 150–200°C, the weak absorption peaks at 1740, 1370, 1210 cm^{-1} could indicate a release of acetone (CH_3COCH_3) [16]. The gas spectrum at 250°C shows broadening of the band around 1800–1665 and shifting of the peak position from 1740 cm^{-1} to 1755 cm^{-1}. The changes observed could be caused by the vibrations of the COO^- group [18]. Probably, in addition to acetone, the evolution of isopropyl acetate ($CH_3COOCH(CH_3)_2$) occurs, as shown by a strong absorption peak at 1755 cm^{-1} . Unfortunately, the other characteristic vibrations of isopropyl acetate and acetone are overlapping. According to the EGA-MS results of Campostrini *et al*. [12], the evolution of isopropyl acetate was observed from TTIP modified by acetic acid.

In addition, at 250°C the intensity of the peaks in the region of 1500–1100 cm^{-1} is enhanced together with those observed at 3100–2700 and 2408–2230 cm^{-1}. New absorptions appear around 1130–926 cm^{-1}. The absorptions at 1061–1100 cm^{-1} are characteristic neither for acetone nor isopropyl acetate. According to the literature data, the evolution of alcohol from stabilized TTIP complexes was observed in the same temperature region [10, 12]. The vibrations in the interval of 1130–926 cm^{-1} could belong to 1-propanol ($CH_3CH_2CH_2OH$) as no characteristic vibrations of other possible gaseous species, e.g. 2-propanol, were detected. Also in this region, the other characteristic vibrations of 1-propanol can not be assigned to the peaks due to the overlapping vibrations of simultaneously evolved gases. The absorptions in the region of 2400–2220 and 759–620 cm^{-1}, belonging to CO_2, become apparent above 200°C (Fig. 5). The vibrations in the region of 2215–2040 cm^{-1} are characteristic for carbon monoxide [16].

The evolution profiles of gases, obtained as derivatives of the peak intensities (dI/dt) or the peak areas (dS/dt), integrated above the baseline, are presented in Fig. 6. For CO and CO_2, the peak areas in the region of 2215–2040 and 2400–2220 cm^{-1}, respectively, were used for the calculations. For acetone, isopropyl acetate and 1-propanol, the intensities of the absorption peaks at 1740, 1755 and 1060 cm^{-1} , respectively, were used for quantitative characterisation.

Acetone, isopropyl acetate and 1-propanol exhibit largely similar evolution profiles. The evolution of acetone and isopropyl acetate starts at temperatures close to 125°C, but that of 1- propanol first at 150°C. The highest evolution rates (Fig. 6) occur between 220–240°C and the intensities of the characteristic peaks reach their maxima at 260–280°C.

The evolution of both CO and CO_2 occurs in two steps (Fig. 6). Although the evolution profiles are almost similar, the processes related to CO_2 are shifted to higher temperatures. CO evolves intensively at 265 and 480°C, while the evolution of CO_2 reaches its maxima at temperatures of 370 and 510°C. The results of evolved gas analysis are also summarized in Table 2. The presence of carbon residues at temperatures below 510°C is evident from the elemental analysis, IR spectra as well as from the color of the sample.

Conclusions

According to IR and MS studies, hydrolysed acetylacetonate-modified TTIP is a monocationic titanium complex consisting of partly hydrolysed isopropoxy groups and acac, which is bidentately bound to titanium, with the main peak at m/z=277.19. Thermal decomposition of the complex in air up to 900°C shows five decomposition steps, resulting in a total mass loss of 43.8%. EGA by FTIR revealed the release of six main gaseous species, *viz*. water, acetone, isopropyl acetate, 1-propanol, carbon monoxide and carbon dioxide. Crystalline TiO_2 anatase phase, free from organic residues, forms around 500ºC and the TiO_2 rutile phase close to 800ºC.

To conclusively determine the composition of the titanium complex and to identify also those evolved gaseous species, which cannot be monitored by IR spectroscopy, additional studies are needed.

Therefore the TG/DTA studies of the complex should be complemented by EGA-MS investigations and then compared to the results of EGA-FTIR, reported in this communication.

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