

TITANIUM(IV) ACETYLACETONATE XEROGELS FOR PROCESSING TITANIA FILMS

A thermoanalytical study

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Thermal decomposition of dried crystalline powder obtained from titanium(IV) bis(acetylacetonate) diisopropoxide (75% solution in 2-propanol) (**1**) was monitored by simultaneous TG/DTA, EGA-FTIR and EGA-MS measurements and the results were compared with those of amorphous powder obtained by gelling of acetylacetonate-modified titanium(IV) tetra-isopropoxide at molar ratio of 1:2 in boiling 2-methoxyethanol (**2**). Thermal degradation of **1** in the temperature range of 25–700°C consists of 5 steps with a total mass loss of 62.5%. EGA by FTIR and MS revealed the release of H₂O below 120°C; followed by an intensive evolution of acetylacetonate around 245°C. The release of acetone and acetic acid occurs up to 270°C and that of CO and CO₂ up to 530°C.

Keywords: EGA by FTIR and MS, sol–gel titania processing, Ti(IV)-acac xerogel

Introduction

Sol–gel processing offers a direct and inexpensive method for the preparation of titania films. To deposit TiO₂ films by sol–gel spray pyrolysis the metal alkoxide precursor needs to be stabilized in order to reduce its reactivity. For that purpose stabilizing agent such as acetylacetonate (acacH) has often been used [1, 2]. Titania films prepared by spray pyrolysis from stabilized metal alkoxide precursors are essential for various high-tech applications, for example UV sensors [1] and solar cells, including dye-sensitized ones (DSSC) [3] as well as extremely thin absorber (ETA) layer solar cells [4]. The better understanding of the thermal behaviour of the gel powders is important in order to optimize the deposition and calcination conditions of the film preparation process [1–4]. Thermal analysis by coupled techniques may be used to monitor the decomposition of titanium(IV) precursors [5–8] in air, thus helping to optimize the calcination conditions of the gels.

Madarász *et al.* have reported on the thermal decomposition of several commercially available chemicals labelled as titanium(IV) oxo-acetylacetonate [7]. They found that the thermal decomposition of the samples studied depends on the degree of crystallinity which is determined by the acetylacetonate (acac) content in the sample. The crystalline samples with higher acetylacetonate concentration (Ti:acac=1:1.8

and 1:1.3) released free acetylacetonate in the temperature range of 240–270°C while the amorphous sample with lower acetylacetonate concentration (Ti:acac=1:0.46) released only a small amount of acacH in the temperature interval of 140–230°C [7].

Earlier we have reported on the thermal degradation including analysis of evolved gases from two different titanium acetylacetonate dried gel powders [5, 6]. These powders were synthesized with two different Ti(IV) isopropoxide (TTIP) and acetylacetonate molar ratios, viz. 1:1 and 1:2, while 2-methoxyethanol (2-MOE) was used as solvent. The gel powders obtained were amorphous and showed somewhat different thermal decomposition. Besides, the gel powder obtained from the sol where TTIP and acacH molar ratio was 1:2 showed a significant release of acetylacetonate [6]. According to EGA-MS both gel powders showed the evolution of gaseous species with $m/z=74$, but the origin of this gaseous species remained unclear. However, if we assume that methoxyethoxy group is present in the structure of the gel powders then unidentified gaseous species could belong to any C₃H₆O₂ compound.

The aim of the present study was to obtain a better understanding of the sol–gel process leading to titania films and the Ti(IV) acetylacetonate (Ti-acac) precursors used therein by exploiting advanced thermoanalytical and other techniques. For this reason and to find the origin of the gaseous species ther-

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mal decomposition of the dried gel powder of the commercial chemical titanium(IV) bis(acetylacetonate) diisopropoxide 75% solution in 2-propanol was studied and compared with the 1:2 sample.

Experimental

Chemicals

Commercially available chemical for synthesis, titanium(IV) bis(acetylacetonate) diisopropoxide 75% solution in 2-propanol (Product No. 843742, Merck, Darmstadt, Germany) and reagent grade chemicals, viz. titanium(IV) tetra-isopropoxide (TTIP) and acetylacetonate (acacH) from Merck (Darmstadt, Germany) as well as 2-methoxyethanol (2-MOE) from Fluka (Steinheim, Germany) were employed. All chemicals were used as received without any further purification.

Synthesis of samples

In order to obtain the dried gel powder (**1**), titanium(IV) bis(acetylacetonate) diisopropoxide (75% solution in 2-propanol) was let to slowly evaporate under ambient conditions. The sol having TTIP:acacH:2-MOE in molar ratios of 1:2:10 was prepared and dried under the same conditions and the obtained powder was labelled as **2**. The preparation procedure of **2** is presented in [6].

Methods

Characterization of the dried gel powders and final products of their decomposition

Elemental composition of the gel powders **1** and **2** was determined by C, H and Ti analyses. C and H analyses were performed in a Heraeus CHN-O-Rapid analyzer at the Microanalytical Laboratory of Eötvös Loránd University of Budapest (ELTE-TTK, Budapest, Hungary). Ti analysis was performed in an inductively coupled plasma mass spectrometer Agilent ICP-MS7500a (Agilent Technologies Inc., USA) at the Laboratories of Tallinn Water Ltd. (Tallinn, Estonia).

XRD patterns of the initial samples and their final products were recorded by X'Pert Pro MPD X-ray diffractometer (Panalytical, The Netherlands) using Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$) and X'celerator detector.

The room temperature micro-Raman spectra of the gel powders were recorded by Horiba LabRam HR800 high-resolution spectrometer equipped with a multichannel detection system in the backscattering configuration. The incident laser light

with the wavelength of 532 nm was focused on samples within a spot of 5 μm in diameter and the spectral resolution of the spectrometer was about 0.5 cm^{-1} .

Thermal analysis

The simultaneous TG/DTA/EGA-MS measurement was performed in an apparatus consisting of an STD 2960 Simultaneous DTA/TGA (TA Instruments, USA) thermal analyzer and a ThermoStar GSD 300 (Balzers Instruments, Switzerland) quadrupole mass spectrometer. Coupling between the two components was provided through a heated (200°C) 100% methyl deactivated fused silica capillary tube with a length of 1 m and inner diameter of 0.15 mm. At first, mass spectra of the evolved gaseous mixtures were continuously scanned and collected between $m/z=1-300$ (SCAN-mode), then 64 mass/charge numbers were selected and ion currents were monitored in multiple ion detection (MID) mode with the measuring time of 0.5 s for each channel. The measurement was carried out in a dynamic air atmosphere using the gas flow rate of 130 mL min^{-1} and the heating rate of $10^\circ\text{C min}^{-1}$.

Evolved gas analysis by TG-EGA-FTIR was performed in the TGA 2050 Thermogravimetric Analyzer (TA Instruments, USA). Gaseous species evolved from the samples were led to FTIR gas cell of a BioRad TGA/IR Accessory Unit equipped with cooled DTGS detector through a heated stainless steel transfer line ($l=90 \text{ cm}$, $d=3 \text{ mm}$) kept at $T=180^\circ\text{C}$. FTIR spectra ($550-4000 \text{ cm}^{-1}$) were collected in every 30 s after accumulation of 29 interferograms by a BioRad Excalibur Series FTS 3000 spectrometer using Win IR Pro 2.7 FTIR (BioRad) data collection and evaluation software. A heating rate of $10^\circ\text{C min}^{-1}$, an air flow rate of 120 mL min^{-1} , (and an extra 10 mL min^{-1} air as a balance purge), and open Pt crucible were used.

The evolved gases were identified on the basis of their MS and FTIR reference spectra available on World Wide Web in the public domain spectral libraries of NIST and SDBS [9, 10].

Results and discussion

Characterization of dried gel powders, **1** and **2**

Raman spectra of the dried gel powders **1** and **2** are presented in Fig. 1. In the case of powder **1**, Raman peaks are well developed and the peaks at 154, 187, 406, 560 and 594 cm^{-1} can be assigned to the (Ti–O–Ti); the peaks at 252, 293, 436 cm^{-1} to the (C–C–O); the peaks at 350 cm^{-1} to the (O–H) and at 943 cm^{-1} to the (CH_3) and/or (C–C–C) vibrations

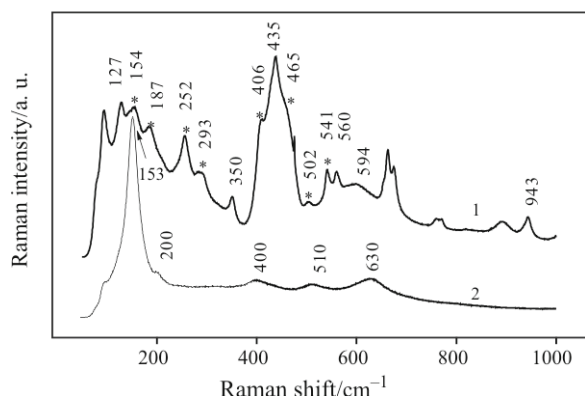


Fig. 1 Raman spectra of the dried gel powders **1** and **2**. The peaks marked with asterisk (*) are close to the Ti–O vibration modes of TiO₂ brookite

[11–14]. Some vibrational bands in spectrum **1** (Fig. 1, marked with asterisk) are also close to the Ti–O vibration modes of TiO₂ brookite [11]. The spectrum **1** is also similar to the Raman spectrum of the commercial solution, titanium diisopropoxide bis(acetylacetonate) 75 mass% in isopropanol; Aldrich Sigma Product No. 325252 [15]. The difference between the solution and the powder **1** is in the region of 100–300 cm⁻¹ which is more defined in the case of powder sample **1**. The spectrum of powder **2** is less resolved than that of **1** showing only broad peaks at 153, 200, 400, 510 and 630 cm⁻¹ which are close to the Ti–O vibrations of the anatase titania [11, 16].

According to XRD, powder **1** is crystalline while powder **2** is amorphous. The XRD reflections of **1** (figure not shown) match very well with the experimental pattern PDF 00-35-1778 (titanium oxo-bis(acetylacetonate) [17], but the pattern is quite different from the reported data for two polymorphs of

titanium oxo-bis(acetylacetonate) (PDF 02-063-6101 and PDF 02-080-2336), whose dimeric structure [Ti₂O₂(acac)₄] has been solved by single crystal X-ray determinations [18]. Sample **1** does not seem to be a mixture of two or more crystalline components, as its XRD pattern occurred in an invariable way also in the samples labelled as TiO(acac)₂ which were studied by Madarász *et al.* [7].

According to elemental analyses, the content of titanium, carbon and hydrogen in the **1** and **2** were found to be 20.28, 40.81, 4.76 mass% and 26.09, 27.76, 3.35 mass%, respectively. Thus, carbon content is higher in crystalline powder **1** which indicates that deficiency of acetylacetonate leads to the amorphous nature of the powder as was also reported by Madarász *et al.* [7]. Based on the titanium mass% we can assume that the theoretical molar masses of **1** and **2** are 236.2 and 183.6 g mol⁻¹, respectively.

An approximate overall composition of **1** is suggested to be TiO_{0.66}(acac)_{1.60}(OH)_{0.87}·0.3H₂O, while TiO_{0.8}(acac)_{0.8}(OH)_{1.6}·0.4H₂O was proposed for **2** [6], taken into account the initial mass losses observed by thermogravimetry (TG) as well.

Thermal analysis

The TG/DTG/DTA curves of sample **1** are presented in Fig. 2. According to DTG, the thermal degradation of sample **1** consists of 5 mass loss steps, whereas 6 mass loss steps were recorded for **2** (Table 1).

The thermal degradation (Fig. 2) of the crystalline sample **1** starts later and all the mass loss steps have maximum at somewhat higher temperatures than those of the amorphous sample **2**, when measured under similar conditions (Table 1). The first decomposi-

Table 1 Decomposition steps, mass losses and temperatures of DTA and DTG peaks of dried gel powders of **1** and **2** as recorded using the heating rate of 10°C min⁻¹ on STD 2960. Simultaneous DTA/TGA thermal analyzer and a Thermostat GSD 300 (Balzers Instruments) quadrupole mass spectrometer

Sample	Step	TG temp. range/°C	Mass loss/%	+/-	DTG _{max} /°C	DTA peak/°C
1	1	25–124	2.0	endo	81	73
	2	124–249	34.2	endo+exo	233	236
	3	249–277	13.1	exo	265	289
	4	277–431	9.2	exo	349	344
	5	431–700	4.0	exo	465	468
	Total mass loss			62.5		
2	1	30–122	4.1	endo	104	107
	2	122–223	15.7	exo	191	198
	3	223–275	10.3	exo	264	271
	4	275–424	15.2	exo	319	323
	5	424–482	5.2	exo	457	459
	6	482–700	3.9	exo	507	507
Total mass loss			54.4			

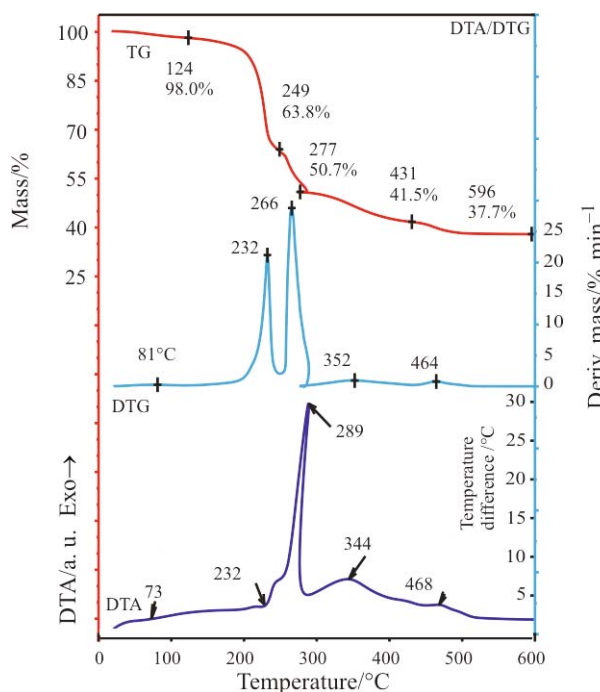


Fig. 2 Simultaneous TG, DTG and DTA curves of **1**. Flowing air: 130 mL min⁻¹, heating rate: 10°C min⁻¹. Sample mass: 17.81 mg

tion step of both samples is in the temperature range of 25–124°C, and for **2** it is recorded as a clear endothermic reaction with two times higher mass loss than that observed for **1**.

There is an initial slow endothermic mass loss (2% up to 124°C) which is most likely due to loss of water. The second mass loss step of sample **1** (Fig. 2) in the interval of 124–249°C starts as an endothermic reaction followed immediately by an exothermic one. The following steps (3, 4, 5) with DTG maxima at 266, 352, 464°C, respectively, are exothermic reactions according to DTA. The mass losses for steps 2 and 3 are 34.2 and 13.1%. In comparison, the dried gel powder **2** shows five mass loss steps (2, 3, 4, 5, 6) after the initial mass loss of 4.1% with DTG maxima at 191, 264, 319, 457, 507°C, respectively, which are all exothermic (Table 1). The main difference in mass losses (Table 1) occurs in the decomposition step 2 where sample **1** exhibits twice the mass loss of sample **2** (15.7%). In the case of **1** we recorded a sudden and huge exothermic heat effect starting at ca. 250°C (Fig. 2). This effect is probably caused by ignition of the already released acetylacetone vapours (see section ‘Evolved gas analysis’) and the TG, DTG and DTA signals are recorded as a function of actual sample temperature and not of the pre-programmed temperature values.

Decomposition of dried gel powders **1** and **2** is practically completed by 520 and 540°C, respectively. The total mass loss in the temperature interval

of 25–700°C is 62.5% for **1** and 54.4% for **2**. Thus, the total mass loss of **1** is significantly higher than that of **2** and can be explained by the higher amount of acetylacetone in **1**.

According to XRD patterns, the final decomposition products of **1** and **2** at 700°C in air consist of crystalline anatase (PDF 00-21-1276) and a mixture of anatase (PDF 00-21-1276) and rutile (PDF 00-21-1272) phases in an approximate ratio of 74:26 [6], respectively. Thus, formation of the rutile phase is favoured from the amorphous and acetylacetone-deficient Ti-acac precursor.

Evolved gas analysis by FTIR

Figure 3 depicts the spectra of evolved gases, obtained by a TG/DTG analysis coupled with simultaneous EGA-FTIR measurements of **1** at temperatures of 245 and 255°C in air. As can be seen, intensive evolution of acetylacetone together with minor evolution of CO₂ takes place at 245°C.

The spectrum obtained at 255°C (Fig. 3) shows continuous evolution of acetylacetone occurring together with an intensive evolution of CO₂. DTA curve of **1** (Fig. 2) indicated exothermic reaction in the temperature interval of 250–290°C due to sudden burning of acetylacetone vapour. According to the FTIR spectra further evolution of CO₂, H₂O, CO and acetic acid occur as the decomposition products of organics in both gaseous and solid phases.

Figure 4 presents the evolution of gases from **1** according to the EGA-FTIR studies. As can be seen, the evolution starts with the release of H₂O around 100°C and then continues with the evolution of

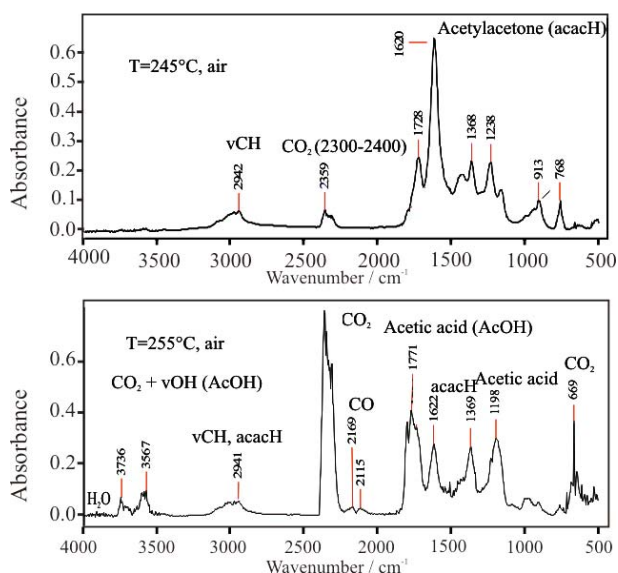


Fig. 3 TG-EGA-FTIR spectra of evolved gases of dried powder **1** at 245 and 255°C. Flowing air: 130 mL min⁻¹, heating rate: 10°C min⁻¹. Sample mass: 46.46 mg

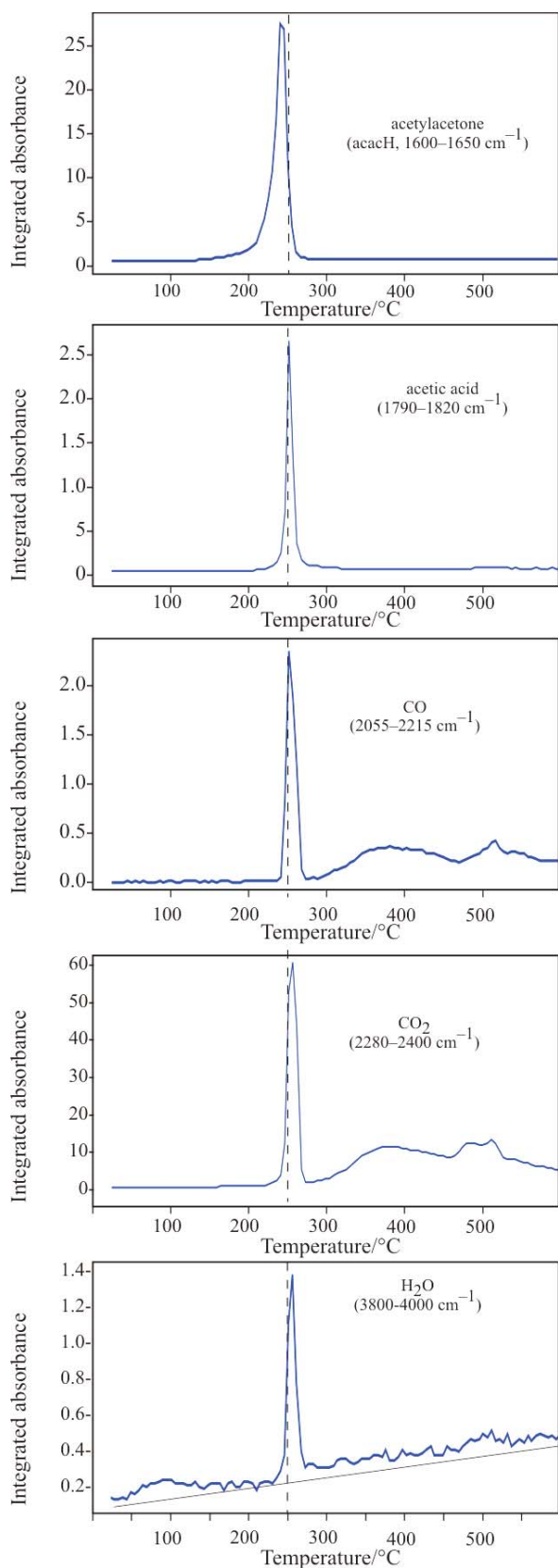


Fig. 4 Evolution profiles of gases as determined by TG-EGA-FTIR of **1**. Flowing air: 130 mL min⁻¹, heating rate: 10°C min⁻¹. Sample mass: 46.46 mg. Dotted line marks the 250°C temperature. Both acetic acid and CO probable come directly from the solid phase

acetylacetonone above 200°C. The evolution of acetic acid together with CO and CO₂ begins at a somewhat higher temperature (250°C) than the maximum evolution of acacH (240°C). This can be compared to our earlier FTIR study of **2** where the corresponding temperatures measured in another apparatus were 300 and 220°C [6].

Evolved gas analysis by MS

Differences in the decomposition of **1** and **2** can clearly be seen by comparing the evolution profiles of evolved gaseous species as recorded by EGA-MS (Fig. 5). The decomposition of both powders starts with the release of H₂O, and its evolution is more pronounced in the case of **2**. This is corroborated by the TG results of **1** and **2** (Table 1) where in the first mass loss step two times higher mass loss was recorded for **2** than for **1**. The overall tendency of the decomposition profiles is that in the case of the crystalline sample **1** the evolution of gaseous species takes place at higher temperatures than with the amorphous sample **2**.

In the second decomposition step (125–250°C) characteristic evolution of acetylacetonone ($m/z=85$), was initiated slightly above 100°C with maximum release at 236 and at 190°C for **1** and **2**, respectively. Approximately two orders of magnitude higher ion current intensity was recorded for **1** despite the fact that the sample mass of **1** was about half of the mass of **2**. This can be explained by the lower acetylacetonate concentration in **2**. In the case of dried gel powder obtained from the sol where Ti(IV) isopropoxide and acetylacetonone molar ratio was 1:1, the evolution of acetylacetonone was detected only in trace amounts [6].

In the second and third decomposition steps of **1** (Fig. 4) and **2** [6] (ca. 120–280°C) the other evolved gaseous species were acetic acid ($m/z=60$), H₂O ($m/z=18$) and CO₂ ($m/z=44$) as also detected by EGA-FTIR. Additionally, the evolution of gaseous species with $m/z=58$ occurs, showing a similar profile of the gaseous species as $m/z=60$ (acetic acid). Gaseous species with $m/z=58$ could be assigned to acetone (CH₃COCH₃) or propylene oxide (CH₃CHOCH₂) [7]. According to EGA-FTIR, the evolution of acetone could neither be definitely identified nor excluded because of possible overlapping of absorption bands with those of acetylacetonone and acetic acid.

Moreover, the evolution of gaseous species with the characteristic m/z value of 74 was detected (Fig. 5). It should be mentioned that evolution of $m/z=74$ starts at higher temperatures than that of acacH, acetone or acetic acid. Gaseous species with $m/z=74$ are evolving in the case of **1** in the tempera-

ture interval of 200–290°C and in the case of **2** in the range of 160–270°C. In our study on the thermal decomposition of **2** [6] we presented the possibility that

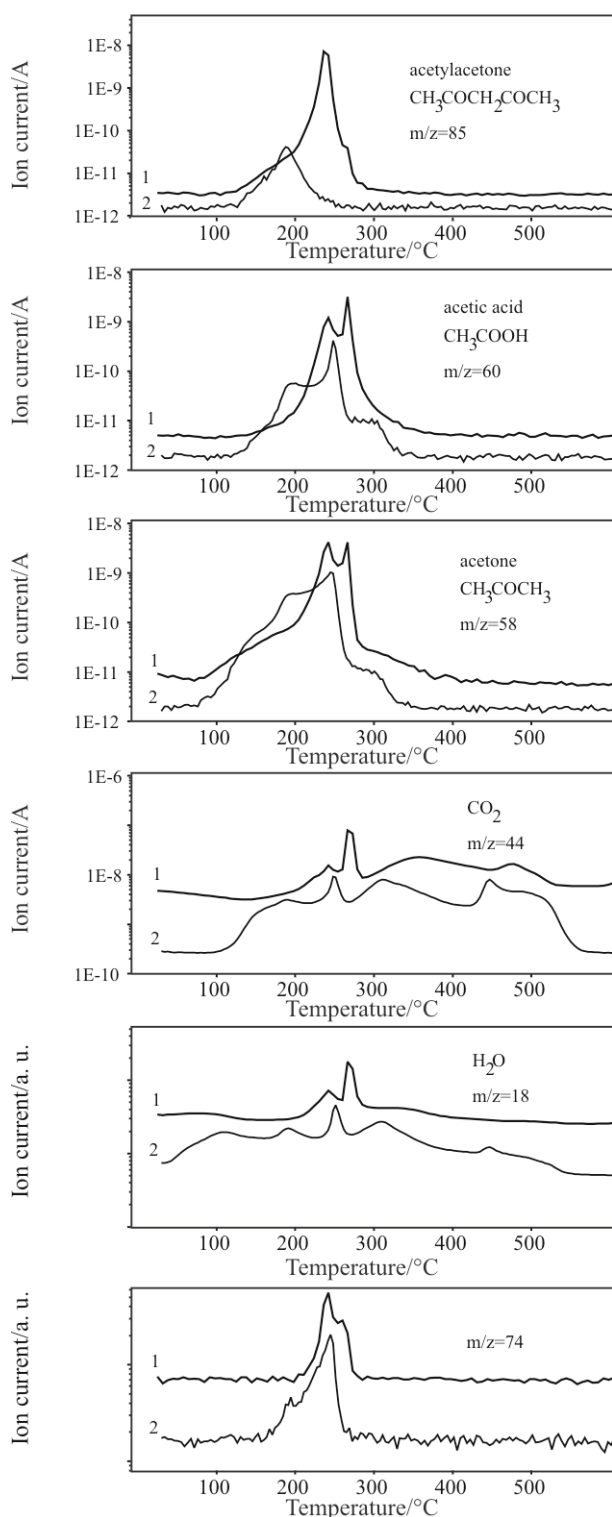


Fig. 5 Comparison of the evolution profiles of gaseous species as monitored by TG/DTA-EGA-MS for the dried gel powders **1** and **2**. Flowing air: 130 mL min^{-1} , heating rate: $10^\circ\text{C min}^{-1}$. Sample mass for **1** – 17.81 and **2** – 33.52 mg

the gaseous species with ion fragment of $m/z=74$ could belong to any $\text{C}_3\text{H}_6\text{O}_2$ compound, viz. 2-methoxy acetaldehyde ($\text{CH}_3\text{OCH}_2\text{CHO}$), propanoic acid ($\text{CH}_3\text{CH}_2\text{COOH}$), ethyl formate ($\text{HCOOCH}_2\text{CH}_3$) and methyl acetate ($\text{CH}_3\text{COOCH}_3$), if we assume that methoxyethoxy group is present in the structure of the dried gel powder [6].

As the evolution of $m/z=74$ was detected also from **1** then its origin can not be 2-MOE. It could be speculated that $m/z=74$ was originating from the reaction between propylene oxide and H_2O .

The evolution of CO_2 and H_2O is recorded up to the end of the decomposition of **1** and **2**. Sample **2** shows more intense evolution of CO_2 than that of **1** in the temperature range of 420–540°C being in agreement with the EGA-FTIR results of **1** (Fig. 4) and **2** [6].

In conclusion, the results obtained by EGA-FTIR coincide with the ones obtained by EGA-MS. However, EGA-MS afforded also the possibility to determine the evolution of acetone and it gave more precise evolution profiles of the gaseous species.

Conclusions

Thermal decomposition of two different titanium acetylacetonate xerogels, first one obtained by drying the commercial titanium(IV) bis(acetylacetonate) diisopropoxide in 2-propanol from Merck (**1**) and the second one from the sol having TTIP:acacH:2-MOE in molar ratio of 1:2:10 (**2**) was studied applying coupled techniques of thermal analysis in air. According to the TG/DTG/DTA curves, all mass loss steps of **1** and **2** in the temperature interval of 120–520°C are exothermic reactions due to the oxidation of organic species accompanied by evolution of CO_2 . Evolution of acetylacetone around 245°C was followed by the release of acetic acid, CO and CO_2 at temperatures around 255°C as recorded for **1** by EGA-FTIR. Our study by EGA-MS complements the list of evolved gases with $m/z=58$ (acetone or propylene oxide) and a gaseous species with $m/z=74$.

When comparing the decompositions of **1** and **2**, the evolved gases are the same but it appears that thermally induced reactions in the case of amorphous acetylacetonate-deficient xerogel **2** occur at somewhat lower temperatures than in the case of **1**. This kind behaviour could be explained by the more ordered and crystalline structure of **1**, also confirmed by the Raman and XRD data. Finally, the result that final solid products at 700°C in air depend on the precursor being anatase for **1** and the mixture of rutile and anatase for **2**, should be considered when choosing the precursors to prepare titania films.

As gaseous species with $m/z=74$ were evolved from both precursors **1** and **2**, then these species can not be originating from the 2-MOE ligand which, according to the NMR spectra, was coordinated to Ti(IV), but present in only trace amount.

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References

- M. Okuya, K. Shiozaki, N. Horikawa, T. Kosugi, G. R. A. Kumara, J. Madarász, S. Kaneko and G. Pokol, *Solid State Ionics*, 172 (2004) 527.
- I. Oja, A. Mere, M. Krunk, R. Nisumaa, C.-H. Solterbeck and M. Es-Souni, *Thin Solid Films*, 515 (2006) 674.
- M. Okuya, K. Nakade, D. Osa, T. Nakano, G. R. Asoka Kumara and S. Kaneko, *J. Photochem. Photobiol. A: Chem.*, 164 (2004) 167.
- M. Krunk, A. Katerski, T. Dedova, I. Oja Acik and A. Mere, *Sol. En. Mat. Sol. Cells*, 92 (2008) 1016.
- M. Krunk, I. Oja, K. Tõnsuaadu, M. Es-Souni, M. Gruselle and L. Niinistö, *J. Therm. Anal. Cal.*, 80 (2005) 483.
- I. Oja Acik, J. Madarász, M. Krunk, K. Tõnsuaadu, D. Janke, G. Pokol and L. Niinistö, *J. Therm. Anal. Cal.*, 88 (2007) 557.
- J. Madarász, S. Kaneko, M. Okuya and G. Pokol, *Thermochim. Acta*, doi: 10.1016/j.tca.209.01.020.
- R. Camprostrini, M. Ischia and L. Palmisano, *J. Therm. Anal. Cal.*, 71 (2003) 1011.
- NIST Chemistry Webbook Standard Reference Database No 69, June 2005 Release, <http://webbook.nist.gov/chemistry/>
- http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi?lang=eng
- S. J. Rigby, A. H. R. Al-Obaidi, S.-K. Lee, D. McStay and P. K. J. Robertson, *Appl. Surf. Sci.*, 252 (2006) 7948.
- P. D. Moran, A. Bowmaker, R. P. Cooney, K. S. Finnie, J. R. Bartlett and J. L. Woolfrey, *Inorg. Chem.*, 37 (1998) 2741.
- V. Mohaček-Grošev, K. Furič and H. Ivankovič, *J. Phys. Chem. A*, 111 (2007) 5820.
- S. F. Tayyari and F. Milani-Nejad, *Spectrochim. Acta A*, 56 (2000) 2679.
- Titanium diisopropoxide bis (acetylacetonate) 75 mass% in isopropanol (325252, CAS Number 17927-72-9) Raman spectrum, <http://www.sigmaaldrich.com/catalog/search/ProductDetail/ALDRICH/325252>
- J. C. Parker and R. W. Siegel, *J. Mater. Res.*, 5 (1990) 1246.
- International Centre for Diffraction Data (ICDD), Powder Diffraction File PDF-2 Release 2007.
- F. H. Allen, *The Cambridge Structural Database, Acta Crystallogr.*, B58 (2002) 380.

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