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Comparative evolved gas analyses of crystalline and amorphous titanium(IV)oxo-hydroxo-acetylacetonates by TG-FTIR and TG/DTA-MS

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ABSTRACT

Decomposition of crystalline and amorphous titanium(IV)oxo-acetylacetonate chemicals have been studied *in situ* up to 800 °C in flowing air by simultaneous thermogravimetric and differential thermal analysis coupled online with quadrupole mass spectrometer (TG/DTA-MS) and FTIR spectrometric gas cell (TG-FTIR) for the analysis of evolved gases (EGA) in order to get more information about pyrolytic processes taking place at elevated temperatures during smooth TiO_2 layer processing.

Crystalline samples (characterized by XRD, PDF 00-35-1778 reference pattern) are releasing acetylacetone (acacH) vapors already from 140 °C onwards. At 245 °C, after an acceleration of this release process, a huge and sharp exothermic heat effect also occurs and results in additional evolution of acetic acid, CO_2, H_2O, and CO. Minute amount of unidentified volatile species with ion fragments not higher than $m/z = 152$ are also detected up to 285 °C. The remaining organic residues are burning out from the solid phase in two further exothermic stages until 500 °C. While an amorphous hydrated sample (with low acetylacetonate content) releases first 6.6% of water vapor until 140 °C, then acetone and acetylacetone up to 300 °C. Between 215 and 385 °C, some acetic acid, CO_2, and CO is also evolved. Formation of CO_2 is detected till 650 °C. At 800 °C, the anatase: rutile TiO_2-ratio were 11:89 and 84:16 for the well-crystallized and the amorphous sample, respectively.

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1. Introduction

Preparation of highly porous TiO_2 samples either in amorphous, anatase or rutile form is frequently desired, in order to achieve, for instance, an increased photocatalytic efficacy in organic transformations [1] or a high discharge capacity in rechargeable lithium ion batteries [2]. A crucial factor influencing the efficiency of a dye-sensitized solar cell (DSSC) of Grätzel type [3] in light harvesting is the extent of porosity of the TiO_2 thin layer. For purposes of DSSC solar cell fabrication, formation of thin TiO_2 films and layers by spray pyrolysis deposition (SPD) is one of the most desired ways. Nevertheless, as a result of low temperature pyrolytic depositions, the formation of anatase phase with highly porous structure is preferred [4,5], and usually there is also a need for a smooth and continuous titania film placed below the porous layer [5].

As precursors for spray pyrolytic deposition of smooth and continuous titania films, sols of various titanium-alkoxides hydrolyzed slowly with acetylacetone (acacH) [6,7] or solution of titanium(IV)oxo-acetylacetonate are proposed [5]. To determine the pyrolytic temperature to be used and to obtain information on the decomposition processes taking place at elevated temperatures usually methods of thermogravimetry (TG) and differential thermal analysis (DTA) are applied, on the solidified acetylacetonato xerogels [7–9]. To identify and monitor the pyrolytic products and processes at a relatively slow heating rate as a function of temperature the various methods of evolved gas analyses (EGA) of the precursors are also advantageous [8–14]. Several organic acids were also applied to prepare titania precursors as powders or thick mesoporous layers, whose thermal decomposition were followed by various EGA methods [10–13]. Certain amorphous, acetylacetonate hydrolysed Ti-alkoxide xerogels from 2-methoxyethanol as precursors were studied by TG/DTA-FTIR [8,9] and TG/DTA-MS [9] reporting evolution of acetone [8] and also acetic acid [9], respectively. Depending on the increased ratio of acetylacetonate incorporated, even a release of free acetylacetone could be monitored by both EGA-FTIR and EGA-MS methods, and variation in the anatase/rutile ratio at 700 °C was observed by XRD [9].

As a part of our ongoing EGA-MS studies on various precursor materials of porous titania film deposition [15,16] for dye-sensitized solar cell fabrication, we here report a comparative *in situ* evolved gas analysis of crystalline and amorphous titanium(IV)oxo-acetylacetonate precursors originating from two

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commercial sources and having different acetylacetonate content (molar ratio of acetylacetonate: Ti^{4+} significantly higher or lower than 1 for the crystalline and amorphous precursors, respectively). The EGA analyses were carried out by both on-line coupled TG-FTIR gas cell and TG/DTA-MS equipment in flowing air, aiming at preparation of smooth and dense titania films to be applied also in Grätzel type solar cells [3,5]. Application of flowing air atmosphere is favorable (compared to the inert atmospheres) from technical point of view to avoid formation of large amount of tar and char, meanwhile the appropriate (air)purging let us have an opportunity for the identification of first non-oxidized organic volatile products released at the very beginning of thermal degradation process by increasing the effective flash temperature through purging the volatiles away and the gas flow can also transfer them into the coupled detector system. Usually, the first gaseous product released is a key compound in any kind of interpretation of thermal decompositions. In some cases, where several components released at different temperatures, or a mixture of vapors of different flammability, beyond the first, there is a chance for more gaseous products to be identified. Meanwhile, at high temperatures the air flow facilitates the burning out of the organic residues.

Very recently, a similarly detailed comparative thermoanalytical study has been reported on amorphous and crystalline ammonium citratoperoxo–Ti^{4+} complex precursors [12,13], where the crystalline complex could be identified as a known compound with well-defined composition and structure. This is not the present case, where the identity of the crystalline phase is still ambiguous and collection of further information needed to achieve its structural resolution. In the very closely related studies, reported in Refs. [8] and [9], only amorphous precursors with relatively low acetylacetonate content (molar ratio of acetylacetonate: Ti^{4+} less than 1) incorporated have been studied.

2. Experimental

2.1. Samples

Commercially available chemicals labeled as titanium(IV)oxoacetylacetonate have been purchased from Tokyo Kasei Kogyo Co. Ltd., (Japan, Product No.) and Aldrich–Sigma (Product No. 3300833, Lot No. 00408BE). The yellow, finely powdered sample from Japan (Sample **1**) was homogeneous, while the sample from Aldrich–Sigma contained fine orange powder together with coarse reddish-brown particles. Pure, orange colored sample **2** was obtained by careful sieving out the coarse reddish-brown particles. These reddish-brown particles sieved out, have been manually handpicked, powdered, and labeled as sample **3**.

FTIR spectra of samples **1**–**3** were measured by Excalibur Series FTS 3000 (Biorad) FTIR spectrophotometer in KBr between 400 and 4000 cm^{-1}, while their XRD patterns were registered on X′pert PRO MPD (PANalytical, The Netherlands) X-ray diffractometer using Cu Kα radiation with Ni filter.

The CH-elemental analyses in a Vario EL III (Elementar Analysensysteme GmbH, Germany) CHN–O analyser showed the following wt% of carbon and hydrogen as two parallel values: C% 43.64, 43.35 and H% 4.98, 5.04 for yellow Sample **1**; C% 37.52, 37.75 and H% 4.72, 4.55 for orange sample **2**; and C% 20.31, 20.58 and H% 2.98, 3.04 for the reddish-brown sample **3**.

2.2. EGA by coupled TG-FTIR

A TGA 2050 Thermogravimetric Analyzer (TA Instruments, USA) with a heating rate of 10 °C min^{-1}, with air flow rate of 120 mL min^{-1} (and an extra 20 mL min^{-1} air as a balance purge) and sample sizes between 30 and 72 mg in open Pt crucible were used.

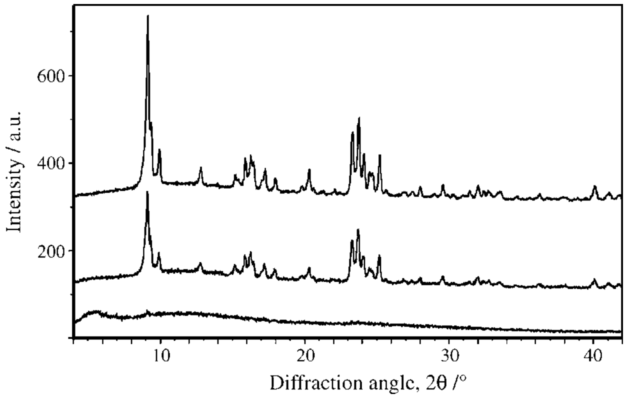

Fig. 1. XRD profile of yellow sample **1** (top), orange sample **2** (middle), and reddish-brown sample **3** (bottom). Crystalline profile of **1** and **2** are in fairly good agreement with experimental pattern of PDF 00-35-1778 [18,19], anyhow sample **1** is more crystalline than sample **2**, while sample **3** is amorphous.

Gaseous species evolved from the samples were led into FTIR gas cell of the BioRad TGA/IR Accessory Unit equipped with cooled DTGS detector through a heated stainless steal transfer line (l = 90 cm, d = 4 mm) kept at T = 180 °C. FTIR spectra (550–4000 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.

2.3. EGA by coupled TG/DTA-MS

A simultaneous thermogravimetric and differential thermal analysis (TG/DTA) apparatus (STD 2960 Simultaneous DTA-TGA, TA Instruments Inc., USA), a heating rate of 10 °C min^{-1}, an air flow rate of 130 ml/min, sample sizes between 11 and 24 mg, and open Pt crucible was used. Mixture of gaseous species could reach the ThermoStar GDS 200 (Balzers Instruments) quadrupole mass spectrometer equipped with Chaneltron detector (EI, 70 eV), through a heated 100% methyl deactivated fused silica capillary tubing kept at T = 200 °C. Data collection was carried out with QuadStar 422v60 software in spectrum scanning (SCAN) mode in the range of m/z = 1–300 and then in Multiple Ion Detection (MID) mode monitoring 64 selected channels ranging mostly between m/z = 15–152. Measuring time was ca. 0.5 s for one channel, resulting in time of measuring of each cycle in ca. 30 s.

2.4. FTIR spectroscopic and mass spectrometric identification of various gaseous species

The components of released gaseous mixtures were monitored and identified mostly on the basis of their FTIR and MS reference spectra available on world-wide web in the public domain spectral libraries of NIST [17].

3. Results and discussion

3.1. XRD characterization of solid oxo-titanium(IV)-acetylacetonate samples 1–3

XRD profiles of samples **1**–**3** are presented in Fig. 1. Samples **1** and **2** show very similar diffraction pattern of a crystalline material, while sample **3** seems to be completely amorphous. The diffraction patterns of samples **1** and **2** are in fairly good agreement with experimental pattern of PDF 00-35-1778, titanium oxobis(acetylacetonate) [18,19] of unknown crystal system, except that the first peak of this reference pattern could not be observed at $2\theta = 4.57°$, whose origin is not known. However, titanium oxobis(acetylacetonate), $TiO(acac)_2$ as a pure compound seems to exist in solid state as a dimer. There are two crystalline modifications of di-μ-oxo-(bis[diacetylacetonatotitanium(IV)]), $[TiO(acac)_2]_2$ (more accurately named as bis(μ_2-oxo)-tetrakis(diacetylacetonato-O,O′)-di-titanium(IV), $Ti_2(\mu\text{-}O)_2(acac)_4$,) with known lattice and molecular structures determined by single crystal X-ray diffraction [20,21]. The crystallographic data and the atomic coordinates are deposited in the Cambridge Structural Database [OXACTI, OXACTI01, 22], furthermore the corresponding calculated powder diffraction patterns are available in the ICDD PDF-4/Organics Database [23]. Unfortunately the generated powder patterns (PDF 02-063-6101 [20,23] and PDF 02-080-2336 [21,23]) of these two known modifications of bis(μ_2-oxo)-tetrakis(diacetylacetonato-O,O′)-di-titanium(IV), $Ti_2(\mu\text{-}O)_2(acac)_4$, are quite different even from the pattern of PDF 00-35-1778 and from the XRD profiles of samples **1** and **2**. As no special variations in the experimental peak intensities are observed, what otherwise would indicate two or more crystalline phase to be present, we can conclude, that the experimental XRD patterns of samples **1** and **2** represent the same single crystalline phase with still unknown structure and composition in the titanium–acetylacetonate systems. Anyhow sample **1** exhibits higher degree of crystallinity (based on peak intensities, and full width half maxima, FWHM values measured under the same conditions) compared to that of sample **2**. It implies that in addition some amorphous phases are also present at least in sample **2**.

A comparison of the theoretical carbon content (47.98%) for the dimeric $Ti_2O_2(acac)_4$, $[TiO(C_5H_7O_2)_2]_2$ with that of samples **1**–**3** given in the experimental part indicates that each of the sample is more or less deficient in its acetylacetonate content. Especially, the measured carbon content of sample **3** is very low. The molar ratio of acetylacetonate: Ti^{4+} is about 1.8, 1.3 and 0.46 for samples **1**, **2** and **3**, respectively. The reasons for the deficiencies compared to the expected theoretical value of 2, are probably originating from the different type of starting materials for titanium, various excess of acetylacetone, and types of solvents applied, furthermore the possibilities for and extent of hydrolysis taking place during the preparation of the samples from different commercial sources should be taken into account. Unfortunately no details on these factors are available. Presence of known types of titanium acetylacetonate crystals containing common additional ligands, such as ethoxy (R = Et), isopropoxy (R = iPr), butoxy (R = nBu) [24,25], either in monomeric $[Ti(acac)_2(OR)_2]$, dimeric $[Ti(acac)(OR)_3]_2$ [24] or tetrameric $[Ti_4(\mu_3\text{-}O)_2(\mu_2\text{-}OiPr)_2(OiPr)_8(acac)_2]$ [25] forms could be excluded by their simulated XRD patterns [22,23].

According to the analyzed carbon contents and the XRD observations, all the samples **1**–**3** seem to be titanium dimers partially hydrolyzed and condensed to various extent. Presence of various amorphous intermediate products of the partial hydrolysis cannot be excluded even in the case of samples **1** and **2** having the same crystalline component, where the overall molar ratio of acetylacetonate: Ti^{4+} is greater than 1, but different, while there are only amorphous products in the case of largely, but not fully hydrolyzed sample **3**, where the overall molar ratio of acetylacetonate: Ti^{4+} is less than 1.

3.2. *FTIR characterization of solid oxo-titanium(IV)-acetylacetonate samples **1**–**3***

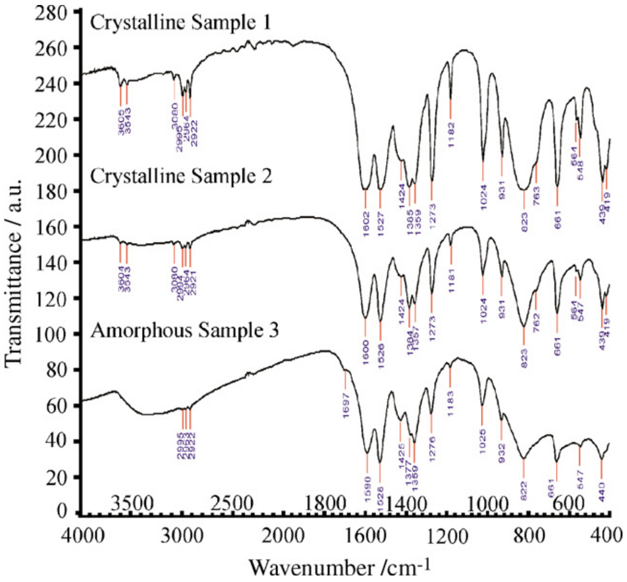

Fig. 2. FTIR(KBr) spectra of yellow, more crystalline sample **1** (top), orange crystalline sample **2** (middle), and reddish-brown amorphous sample **3** (bottom). Sample **3** seems to be strongly hydrated.

FTIR spectra of samples **1**–**3** are shown in Fig. 2. Again the spectra of crystalline samples **1** and **2** are strikingly similar to each other, while that of the amorphous sample **3** is somewhat different at least in the hydrogen-bonding region (2000–4000 cm^{-1}), between 1350 and 1450 cm^{-1}, and in the fingerprint region (<1000 cm^{-1}). Anyhow spectra of all the three samples are consistent with the compounds incorporating acetylacetone in form of chelating acetylacetonate anions. The pair of $\nu(C{=}O)$ stretching bands of chelated acetylacetonates are located at 1602 and 1527 for sample **1**, at 1600 and 1526 for sample **2**, being at 1590 and 1528 cm^{-1} for the amorphous sample **3**. No clues of alkoxide residues can be found in comparison with reference IR spectra of similar crystalline complex species containing alkoxide ligands [24]. Spectra of crystalline samples **1** and **2** exhibit stretching vibrations at 3543 and 3605 cm^{-1} due to free OH groups. The origin of these free OH vibrations is explained by an easy exchange of the second loosely bound acetylacetonate anion of a Ti^{4+} center for a hydroxide ion as a result of partial hydrolysis taken place formerly with H_2O. Simultaneously volatile acetylacetone molecules can be released, as well.

The amorphous sample **3** having an extended hydrogen-bonding system, probably contains a considerable number of water molecules bound in various ways. Intensity discrepancies in the other two regions mentioned above probably come from the amorphous structure of sample **3**. The spectrum of sample **3** is very much similar to the spectra of an amorphous, acetylacetonate hydrolyzed Ti-isopropoxide xerogel precursor obtained from 2-methoxyethanol using 1:1 molar ratio of Ti-alkoxide and acetylacetonate, prepared and studied by Krunks et al. [8]. The $\nu(C{=}O)$ stretching bands of chelated acetylacetonate moieties were found at 1580 and 1530 cm^{-1} [8]. During further studies of this group [9] an approximate composition of such a xerogel free of alkoxide: $TiO_{1.325}(OH)_{0.90}(acac)_{0.45}\cdot 0.78H_2O$ was revealed. Application of 1:2 molar ratio of starting materials resulted also in a hydrated amorphous xerogel $TiO_{0.8}(OH)_{1.6}(acac)_{0.8}\cdot 0.4H_2O$ with a very similar spectrum [9]. Spectrum published in Ref. [7] is also quite similar to that of sample **3**, but it shows an excessive strong absorption band at 1052 cm^{-1}, which indicates incorporation of n-butoxide into that xerogel [7].

In summary, all samples, *viz.* the crystalline **1**–**2** and amorphous **3**, can be considered as solid solutions and/or mixtures to a less or higher extent, i.e. partially hydrolyzed (and oligomerized), acetylacetonate anion (acac)-deficient, but hydroxide (OH^-)-enriched, probably non-stoichiometric titanium(IV)oxo-hydroxo-acetylacetonates, respectively. One of the components seems to be present in the same crystalline form both in samples **1** and **2**. The approximate average composition for the mainly crystalline and amorphous samples (**1**–**2** and **3**, respectively) could be calculated

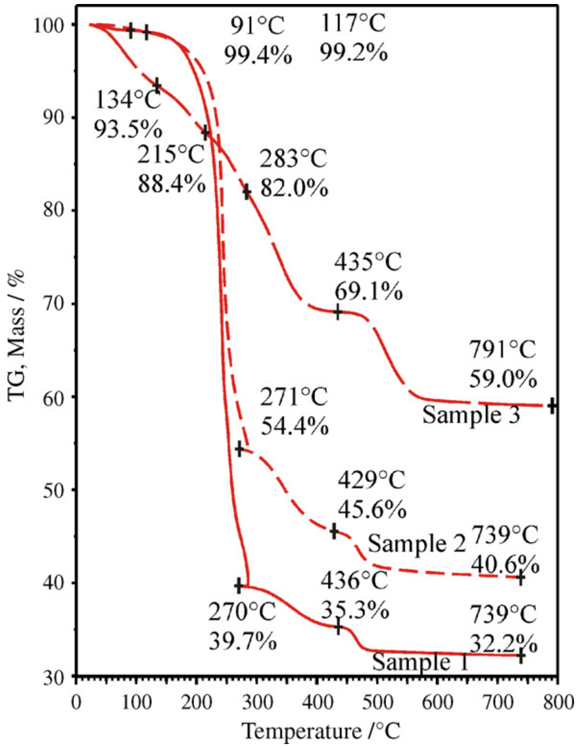

Fig. 3. TG curves of the more crystalline sample **1** (solid line), crystalline sample **2** (short dashed line), and amorphous sample **3** (long dashed line) in simultaneous TG/DTA measurements in an air flow of 130 ml/min at 10 °C/min heating rate (initial masses are 12.62, 23.12, and 11.89 mg, respectively).

by combining the results of C and H-analyses and their water and Ti-contents measured by thermal analysis (the latter e.g. in form of TiO_2 formed during thermal decomposition of samples in air). To give an estimate on the particular composition of these samples studied is especially important if we would like to explore the identity of crystalline phases prepared probably from concentrated solutions and observed by XRD in samples **1** and **2**, and to compare their thermal behavior to the amorphous xerogel phases (sample **3**) formed from similar solutions under more intense or more prolonged conditions of hydrolysis and condensations, similarly as in cases of Ref. [12]. We would like to extend our investigation into such mysterious and ill-defined chemicals, to encompass similar products obtainable from other suppliers, as well [26].

3.3. *Thermal behavior of samples **1**–**3** in the simultaneous TG/DTA apparatus*

In comparison, the simultaneous thermogravimetric (TG) and the corresponding differential thermal analytical (DTA) curves of the samples are shown in Figs. 3 and 4. The main features of the mass loss curves (TG) are quite similar for the crystalline samples **1** and **2**, while they are quite different from those of the amorphous sample **3**. The same can be stated about the corresponding DTA curves, too. According to the TG curves (Fig. 3), a gradual decomposition of amorphous sample **3** starts at almost room temperature, while crystalline sample **1** and **2** shows a sudden and sharp weight loss step only between 150 and 280 °C. Above 280 °C two additional decomposition steps occur in both cases up to 500–600 °C. Each thermal degradation step is accompanied by exothermic heat effects, except those below 100 °C (DTA curves, Fig. 4). In the case of samples **1** and **2** the main decomposition step is escorted by a very huge exothermic heat effect, which causes a local overheating of samples and an unusual, but still rather typical shape of TG and DTA curves recorded as function of sample temperature (Figs. 3 and 4). The transformation of amorphous decomposition products in anatase takes place when the last large portion of organic residues is burning out. It is marked by a unified exothermic heat effect of burning and transformation peaked at around 470 °C and 520 °C for samples **1**–**2**, and **3**, respectively.

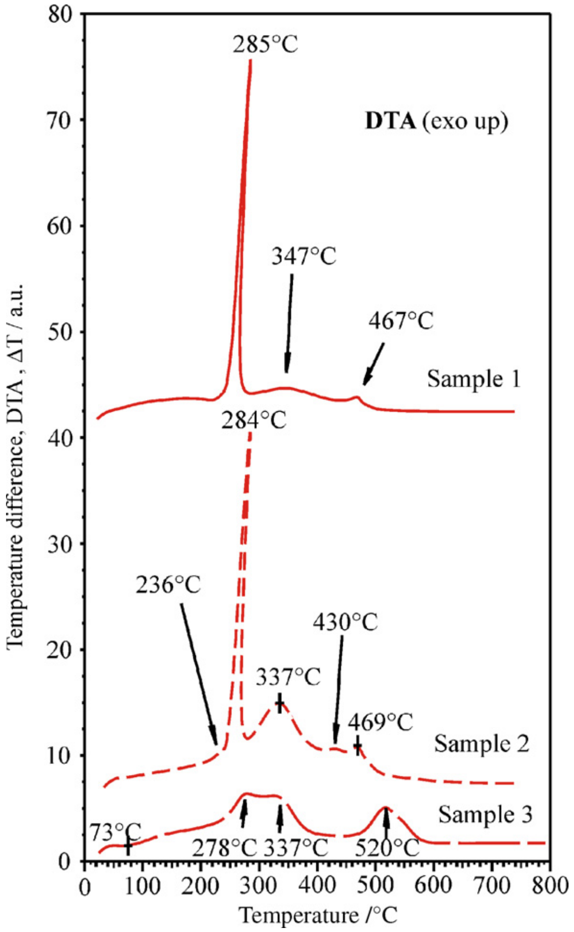

Fig. 4. DTA curves of the more crystalline sample **1** (solid line), crystalline sample **2** (short dashed line), and amorphous sample **3** (long dashed line) in simultaneous TG/DTA measurements in an air flow of 130 ml/min at 10 °C/min heating rate (initial masses are 12.62, 23.12, and 11.89 mg, respectively).

Above 750 °C, the stabilization of sample masses indicates completion of the formation of TiO_2. The amount of remaining titania is found in the TG/DTA-MS crucible to be 32.2, 40.6, and 59.0% for samples **1**–**3**, respectively, while for sample **2** in the TG-FTIR run (not shown) a residue of 38.7% was observed. In agreement with the results of organic elemental analysis, the higher organic carbon content is accompanied with a lower titanium (titania) content. Assuming no significant loss of titanium during the decomposition processes and combining the results of C and H-analyses for acetylacetonate content with the measured titanium (titania) content, and also considering the water released below 100 °C, the following approximate overall or average composition of the samples could be calculated by regression (taking into account the mass balances for Ti, C, H and O elements and electron neutrality and assuming Ti^{4+} state, there is no reason for assuming of Ti^{3+}):

- $TiO_{0.83}(acac)_{1.80}(OH)_{0.54}\cdot 0.088H_2O$ for sample **1**;
- $TiO_{0.86}(acac)_{1.30}(OH)_{0.98}$ for sample **2**; while
- $TiO_{1.525}(acac)_{0.46}(OH)_{0.49}\cdot 0.49H_2O$ for amorphous sample **3**.

Samples **1** and **2** have significantly higher acetylacetonate content (1.8 and 1.3), than sample **3** has (0.46) in units mol per mol

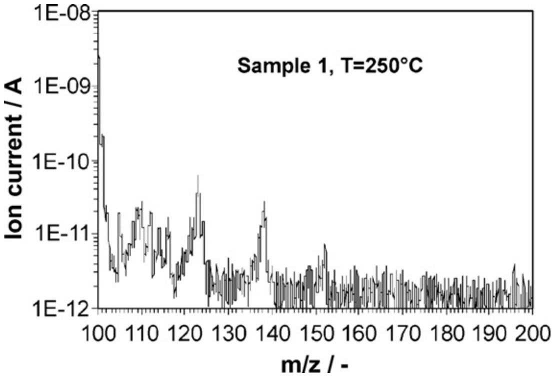

Fig. 5. Mass spectrum segment of the more crystalline sample **1**, measured at $T = 250\,^{\circ}C$ between $m/z = 100$ and 200 by *in situ* online coupled TG/DTA-EGA-MS system (10 °C/min heating rate, 130 ml/min air flow, initial mass 12.62 mg).

Ti. The acetylacetonate anion deficiency is compensated in each calculation with hydroxide ions, which can definitely be assumed based on their FTIR spectra, and which are considered as products of hydrolysis (acac-Ti. . . + H_2O = HO–Ti. . . + acacH).

The formulas given here are strictly comparable only in their acetylacetonate anion content, while two hydroxide anions is equivalent having one water molecule and one oxygen dianion, and vice versa. For example, if we consider the theoretical composition of $TiO_{1.5}(acac)_{0.5}(OH)_{0.5}\cdot 0.5H_2O$, it is equal to $TiO_{1.0}(acac)_{0.5}(OH)_{1.5}$ or to $Ti_4O_4(acac)_2(OH)_6$. The latter formulae may correspond to a more hydrolyzed and meanwhile further dimerized, i.e. tetrameric species $[Ti_4(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(OH)_6(acac)_2]$ having very similar basic (ladder-like) skeleton as that of $[Ti_4(\mu_3\text{-}O)_2(\mu_2\text{-}OiPr)_2(OiPr)_8(acac)_2]$ crystal [25]. Considering that the amorphous sample **3** and one of the samples in Refs. [8] and [9] have a composition quite close to the molar ratio of Ti^{4+}:acetylacetonate = 1:0.5 = 4:2, such ladder-like tetrameric $[Ti_4(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2]$ cores [25] might be (though random associations therein) the structural basis of such amorphous hydroxo-oxo-titanium-acetylacetonate xerogels.

An intermediate hydrolysis product (through acac-OH replacement) starting from the dimeric $Ti_2(\mu\text{-}O)_2(acac)_4$ towards $[Ti_4(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(OH)_6(acac)_2]$ might condense in a more symmetric but similar tetrameric species, $[Ti_4(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(OH)_4(acac)_4]$ = TiO(acac)(OH), which might be also a possible candidate to describe the crystalline phase observed in the samples **1** and **2**.

The ratio of anatase to rutile contents (rutile, PDF 00-21-1272) and anatase, PDF 00-21-1276 [18]) is varying, according to a semi-quantitative analysis of the XRD patterns of titania residues applying the reference intensity ratio (RIR) method [27], as follows. Residue of sample **1** showed preferred rutile formation in 25:75 and 11:89 ratio at 750 and 800 °C, respectively. While residue of sample **2** contained titania-modifications preferring anatase in 60:40 ratio at 750 °C, but residue of sample **3** showed even a higher anatase/rutile ratio of 84:16 even at 800 °C. It seems, that an early and intense burning out of the organic residues helps to lower the anatase formation temperatures, which facilitates also the formation of rutile from anatase structure. The latter process seems to be related to the final removal of the minute residual contaminations, which usually are taking place continuously in the approximate temperature range of 600–800 °C, as demonstrated also by high-temperature HT-XRD [12]. In case of amorphous sample **3**, the burning processes of organic parts are relatively slow and elongated, and not so complete as in the case of samples **1**–**2**, what seems to have resulted in the lowest rutile to anatase ratio even at 800 °C.

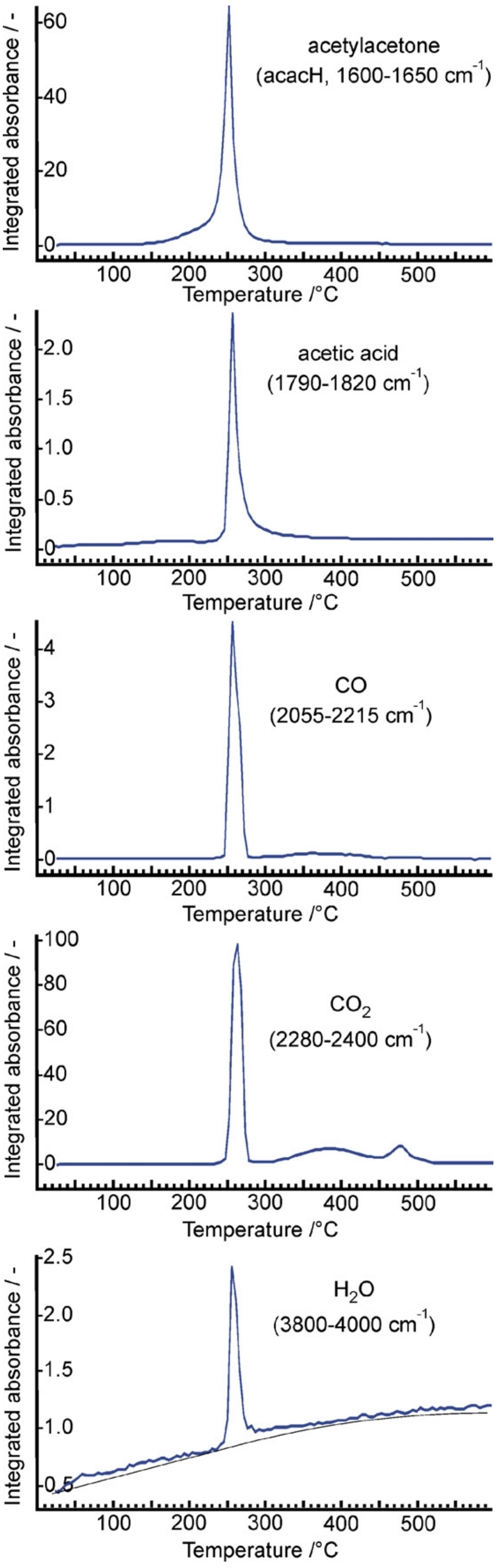

Fig. 6. Evolution courses of gaseous species (acetylacetone, acetic acid, CO_2, CO, and H_2O, from top to bottom) from the more crystalline sample **1** as observed in *in situ* TG-EGA-FTIR measurement. (By integration of absorbance in their characteristic wavenumber regions, 10 °C/min heating rate, 140 ml/min air flow, initial mass 41.84 mg.)

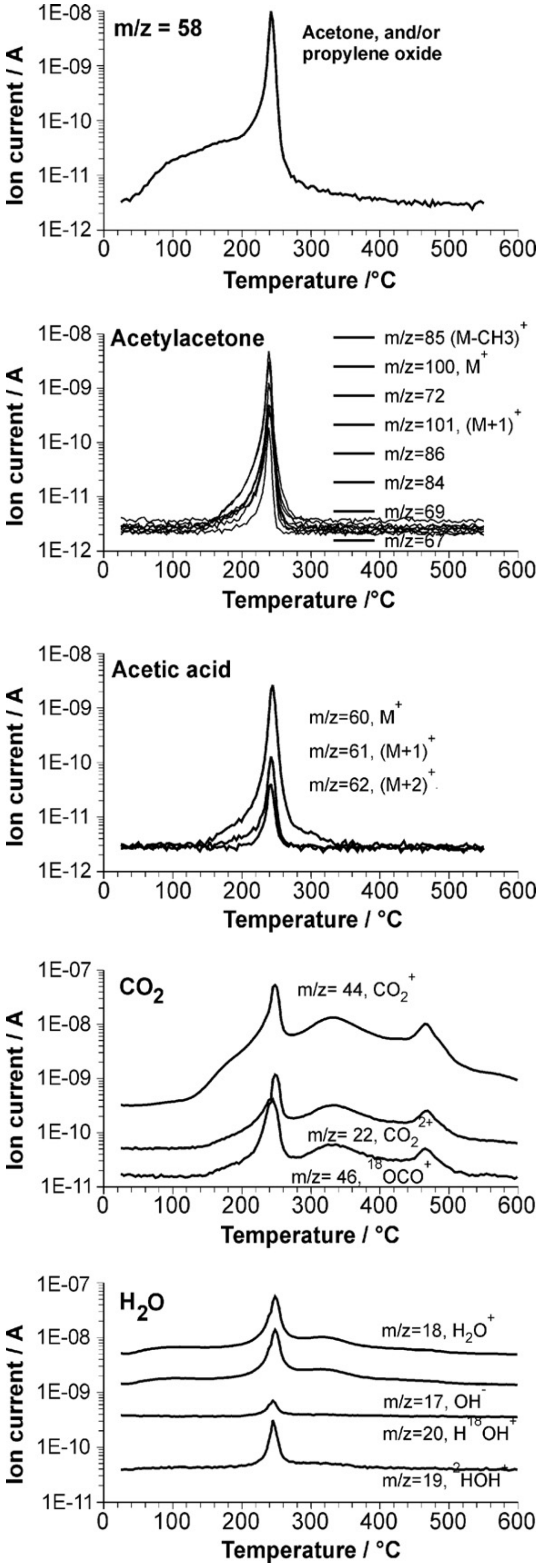

Fig. 7. Gas-evolution represented by curves of selected mass-spectroscopic ion-currents of $m/z = 58$, acetylacetone, acetic acid, CO_2, and H_2O released from the crystalline sample **2**, measured by online coupled TG/DTA-EGA-MS system (air flow 130 ml/min, heating rate 10 °C/min, initial mass 23.12 mg). Displaying of logarithmic curves of several fragment ions, including double charged and natural isotopes demonstrates the merit and sensitivity of the MS-measurement system applied.

*3.4. Evolution of gaseous species from crystalline samples **1** and **2** measured in situ by TG-FTIR spectrometric gas cell and TG/DTA-EGA-MS system*

The scanned EGA-MS spectra of samples **1** and **2** usually showed ion fragments only with m/z values less than 103 unit, except the spectra from temperature range of 240–270 °C of their main decomposition stage, in which some additional ions with m/z value between 103 and 153 have also occurred (Fig. 5). The absence of ions with $m/z > 153$ value, the absence of an ion fragment with $m/z = 147$ (which might correspond to Ti-acac$^+$, the smallest fragment from a hypothetic volatile Ti-acac$_x$ species), and also the lack of observation of groups or sets of ions corresponding the natural abundance of Ti isotopes, altogether indicate, that probably no volatile species with Ti content has been released. Ions with $m/z > 102$ might be explained by some volatile organic condensation products, which unfortunately could not be identified.

Individual gaseous products evolving from the decomposing samples **1** and **2**, with $m/z < 102$ were identified mainly with help of the corresponding FTIR spectra series measured by TG-EGA-FTIR-gas cell (Fig. 6). The combined analysis has confirmed, that these crystalline samples are releasing freed acetylacetone (acacH) vapors already from 140 °C, which is actually the boiling point of acacH. Release of adsorbed excess of acetylacetone, what might be expected to occur below this boiling point, is not observed at all. Anyhow, between 140 and 220 °C, an escape of occluded acetylacetone as product of former hydrolytical processes cannot be excluded. Nevertheless, between 220 and 280 °C, the observed intense evolution of pure acetylacetone is most likely the consequence of a one-proton (H^+) migration to acetylacetonate anions from a neighbouring anion (which latter one becomes double negatively charged), or from OH or H_2O groups still present. At 245 °C, after the acceleration of release rate of acacH, in addition, some evolutions of acetic acid, CO_2, H_2O, and CO has also occurred (Fig. 6). By careful checking the peak temperatures of EGA-FTIR traces (zooming in is not shown) we can also draw some conclusions on the allocation and differentiation of solid phase thermal processes and products of degradation and gas phase oxidation. Oxidation of acacH vapors may result mainly in CO_2 and H_2O formation, meanwhile acetic acid and CO might be the degradation products of organic double charged anions remained in the condensed phase. Unfortunately, CO could not be monitored in a reliable way in air by EGA-MS. Furthermore, acetic acid may be also one of the pyrolytic products of free acacH [28], although its tailing type evolution curve indicates rather its formation from condensed residues. In case of Sample **2**, evolution of acetone was observed at least from 80 °C by both EGA-FTIR and EGA-MS.

Beyond acetic acid, Charles et al. [28] identified also acetone at 346 °C as an other pyrolytic product of pure acetylacetone, while von Hoene et al. [29] found acetone among the pyrolysis products of a wide variety of metal acetylacetonates even at about 250 °C by MS. Formation of acetone from sample **1** or **2**, between 240 and 270 °C could not be definitely confirmed by EGA-FTIR spectra evaluation, because of strong overlappings in vapor spectra of acetone and acetylacetone (acacH) [17], while it could not be excluded by evaluation of EGA-MS spectra, because of the occurrence of $m/z = 58$ (M^+ of acetone) with definitely higher intensity as expected from the reference MS-spectra of acacH [17] in both cases. This discrepancy might be resolved by assumption of a formation of propylene oxide [$CH_3CH(O)CH_2$] instead of acetone by 250 °C. IR spectra of propylene oxide vapor [17] can be hardly traced because of its very low absorption coefficients, meanwhile its mass of molecular ion is the same ($m/z = 58$, M^+) as that of acetone in MS. Consequently, Py-GC–MS methods are needed to resolve this uncertainty.

Evolution course of gases, represented by curves of selected mass-spectroscopic ion-currents of decomposition products (such

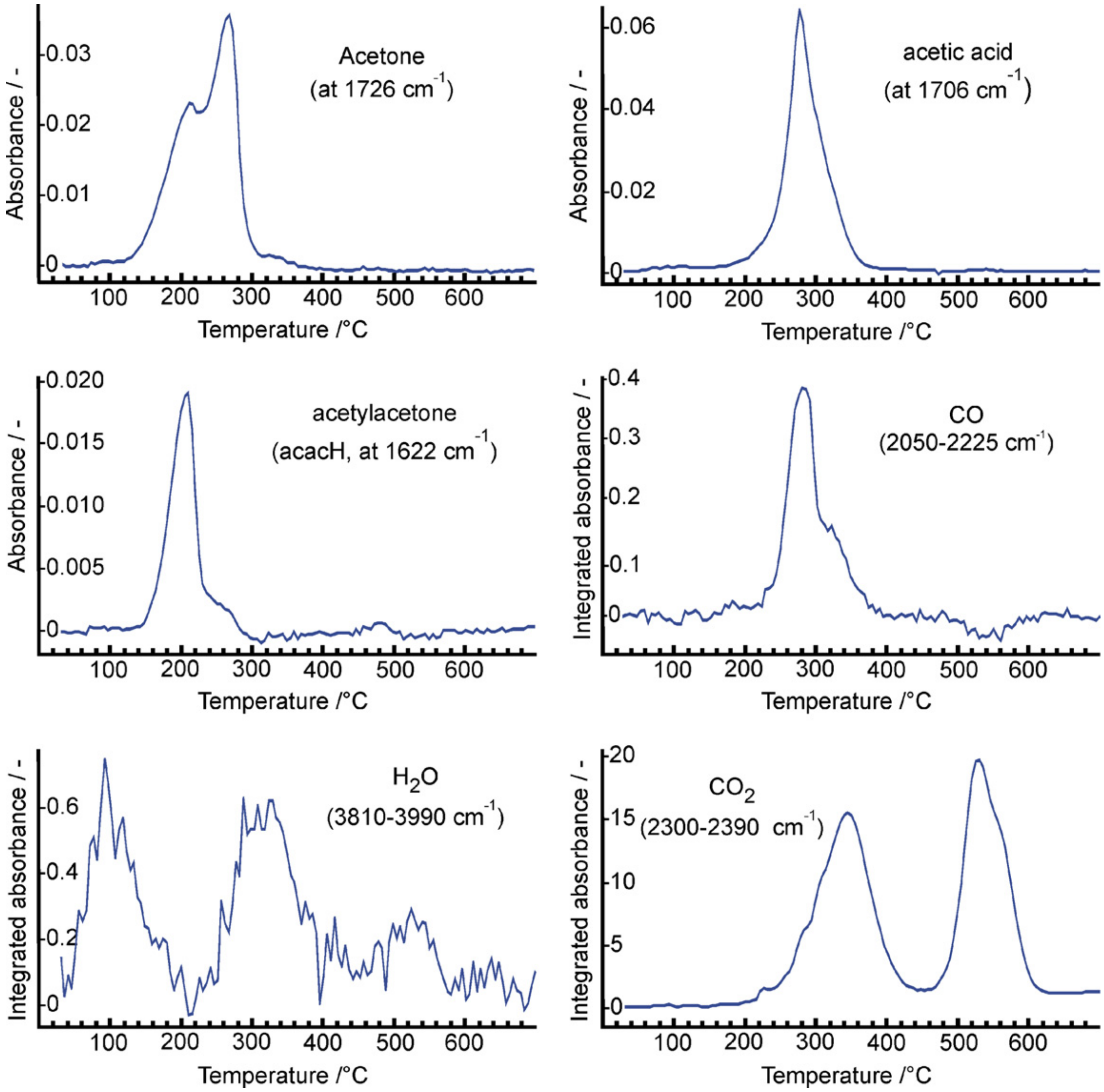

Fig. 8. Evolution courses of gaseous species (H_2O, acetone, acetylacetone, acetic acid, CO, and CO_2) from the amorphous sample **3** as observed in the *in situ* TG-EGA-FTIR measurement. (Curves are created by integration of absorbance in their characteristic wavenumber regions; 10 °C/min heating rate, 140 ml/min air flow, initial mass 30.06 mg.)

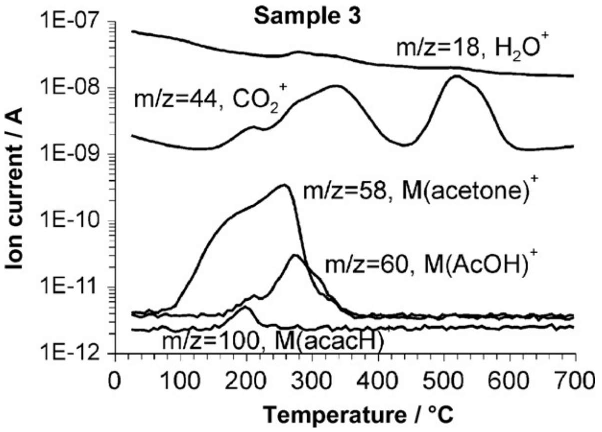

Fig. 9. Representative mass spectroscopic gas-evolution curves of molecular ion of acetone, acetic acid (AcOH), acetylacetone (acacH), CO_2, and H_2O released from the amorphous sample **3**, measured by online coupled TG/DTA-EGA-MS system (air flow 130 ml/min, heating rate 10 °C/min, initial mass 11.89 mg).

as acetone and/or propylene oxide, acetylacetone, acetic acid, CO_2, and H_2O, except CO) released from crystalline sample **2** and measured by the online coupled TG/DTA-EGA-MS system, are shown in Fig. 7.

*3.5. Evolution of gaseous species from amorphous sample **3** measured in situ by TG-FTIR spectrometric gas cell and TG/DTA-EGA-MS system*

MS spectra of hydrated amorphous sample **3** did not contain any ion fragments with mass per charge ratio $m/z > 103$, that is, no volatile Ti-acac$_x$-species are released during its decomposition, which started with evolution of water vapor and followed by that of acetone from 130 °C together with a small amount acetylacetone (Fig. 8) from 150 °C.

Evolution of acetone was dominating between 130 and 300 °C in two stages, while the evolved amount of acetylacetone was already decreased above 230 °C, meanwhile the evolution of acetic acid, CO, H_2O, and CO_2 has occurred. Above 400 °C only evolution of CO_2 has taken place up to 650 °C. Similar evolution of acetone and acetic acid vapors were also reported by Oja-Açik et al. [9] from two amorphous Ti(IV)oxo-acetylacetonates, while acetylacetone evolved only from sample with approximate composition of hydrated amorphous xerogel $TiO_{0.8}(OH)_{1.6}(acac)_{0.8}\cdot0.4H_2O$ and not from sample $TiO_{1.325}(OH)_{0.90}(acac)_{0.45}\cdot0.78H_2O$ [9]. The EGA-MS measurements (Fig. 9) have also confirmed the evolution of relatively small amount of acetylacetone (among the other products) from sample **3**, resembling in this respect the latter sample of Ref. [9].

4. Conclusion

Commercial titanium(IV)oxo-acetylacetonate samples studied are proven to be titanium(IV)-oxo-hydroxo-acetylacetonates with various acetylacetonate content. Samples with Ti:acac ratio of 1:1.8 and 1:1.3 (sample **1** and **2**, respectively) showed the same crystalline phase as major part, meanwhile of 1:0.46 (sample **3**) was found completely amorphous. Considering also further observations [8,9,26], we suggest that samples with a rather high acetylacetonate content are more likely crystalline, and those of with low content of acetylacetonate tend to be amorphous, however this is not proven. Sample **1** and **2** with higher acetylacetonate content release suddenly between 240 and 270 °C free acetylacetone, which catch fire also producing highly exothermic heat effect. Some oxidative degradation products, such as acetic acid, CO, and some volatile condensation products with ion fragments of m/z as high as 103–156 have also occurred.

The hydrated amorphous sample **3** with low acetylacetonate content released water below 140 °C, acetone and small amount of acacH between 140 and 230 °C, then acetone and acetic acid between 230 and 300 °C. The organic residues are burned out totally below 500 °C for samples **1** and **2**, while only above 560 °C for sample **3**. At 750–800 °C the titania residues contain mainly rutile for sample **1**, meanwhile preferably anatase is observed for samples **2** and **3**. Considering requirements such as purity, anatase form of smooth titania films, and low deposition temperature, sample **2** seems to be optimal precursor, as the films prepared thereof can become relatively free from organic impurities already by 500 °C and meanwhile could exhibit mainly well-crystallized anatase form of titania. Anyhow, the final quality of semiconductive smooth films is often a compromise between the high chemical purity and the requested activity, the latter being usually bound to a high level of crystal/lattice defects of usually extrinsic origin.

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