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THERMOANALYTICAL STUDIES OF TITANIUM(IV) ACETYLACETONATE XEROGELS WITH EMPHASIS ON EVOLVED GAS ANALYSIS

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Thermal decomposition of precursor xerogels for TiO_2, obtained by gelling of acetylacetonate-modified titanium(IV) tetraisopropoxide (prepared at Ti-alkoxide:acetylacetone molar ratios of 1:1 (Ti-1) and 1:2 (Ti-2)) in boiling 2-methoxyethanol, was monitored by simultaneous TG/DTA/EGA-MS and EGA-FTIR measurements. Thermal degradation processes of Ti-1 and Ti-2 in the temperature range of 30–700°C consist of six mass loss steps, the total mass loss being 46.3% and 54.4%, respectively. EGA by FTIR and MS revealed release of H_2O below 120°C; followed by evolution of acetone and acetic acid between approximately 100 and 320°C, and that of CO_2 up to 560°C. Acetylacetone is evolved to a significant extent from sample Ti-2 at 120–200°C.

Keywords: *EGA-FTIR, EGA-MS, simultaneous TG/DTA, sol–gel, titania, titania-xerogels*

Introduction

The sol–gel process allows the preparation of homogeneous materials with controlled structure-property characteristics by chemically modifying the precursor systems [1]. TiO_2 films prepared by the sol–gel method have attracted wide interest as dielectric, photocatalytic and photovoltaic materials [2–5].

Ti-alkoxides are commonly used precursors for titania in spite of their being easily hydrolysed. Their reactivity can be controlled by using chemical modifiers, e.g. formic, oxalic and acetic acids or acetylacetone [3, 6–10].

The present study is a continuation of our previous investigations into the thermal behaviour of titanium xerogels [11]. We focus here on comparing thermal behaviour of dried titanium gels prepared at two different molar ratios from titanium tetra-isopropoxide (TTIP) and acetylacetone (acacH), *viz.* 1:1 and 1:2, diluted in 2-methoxyethanol. It must be pointed out that the xerogel formed and its thermal degradation process can be rather complicated if 2-methoxyethanol (2-MOE) is used as solvent, because 2-MOE is known to be a strong chelating agent [12]. According to our earlier studies, smooth and dense TiO_2 films can be deposited from this precursor solution, however [13].

The thermal degradation of titania xerogels was followed by simultaneous TG/DTA/EGA-FTIR and TG/DTA/EGA-MS measurements in flowing air in the temperature range of 30–700°C using the heating rate of 10°C min^{-1}. In our previous work [11], the 1:1 titania xerogel was synthesised by a similar route but the thermal degradation process was monitored with the heating rate of 5°C min^{-1}.

The aim of the work was to obtain by advanced thermoanalytical techniques a deeper understanding of the sol–gel deposition process for titania thin films employing acetylacetonate-stabilized titanium isopropoxides in 2-methoxyethanol as precursors.

Experimental

Materials

Chemicals

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

Synthesis of the samples

Acetylacetone was added dropwise to TTIP in molar ratios of 1:1 and 2:1. The solutions were stirred for 30

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min at room temperature. The stabilized TTIP solutions were thereafter mixed with 2-MOE (in a molar ratio of 1:10) and the mixture was refluxed at 130°C for 2 h. The final solutions were cooled down to room temperature. To obtain the xerogel, the solution was allowed to slowly evaporate under ambient conditions. The xerogels, used as samples for the thermal analysis, were labeled as Ti-1 (TTIP:acac=1:1) and Ti-2 (TTIP:acac=1:2).

Methods

Characterization of the xerogels and final products of their thermal decomposition

Elemental composition of the xerogels was determined by C and H analyses of the Ti-1 and Ti-2 samples, performed in a Heraeus CHN-O-Rapid analyzer at the Microanalytical Laboratory of Eötvös Loránd University of Budapest (ELTE-TTK, Budapest, Hungary).

FTIR absorption spectra of the powdered samples were recorded in the region of 4000–400 cm^{-1} on a Perkin Elmer GX1 spectrometer using the KBr pellet technique.

XRD patterns of the initial samples and those of the titania products, obtained at 700°C in the thermal balances, were recorded by X'Pert Pro MPD X-ray diffractometer (Panalytical, The Netherlands) using Ni-filtered CuK_{α} radiation. The phase analyses were carried out with the X'Pert HighScore Plus (ver. 2.2) search/match software.

Thermal analysis

TG/DTA measurements, coupled with the evolved gas analysis by FTIR (EGA-FTIR), were carried out in the Setaram Labsys 2000 instrument using the heating rate of 10°C min^{-1} and air flow rate of 130 mL min^{-1}, open Pt crucibles and a sample mass of 33.4 mg (Ti-1) or 37.3 mg (Ti-2). Before the TG/DTA/EGA-FTIR measurements, additional heat treatments of the samples were performed on a preparative scale in air using a Nabertherm laboratory oven. The heat treatment was performed up to 120°C with the heating rate of 10°C min^{-1}. The necessity of the precursor pre-heat treatment is discussed in our earlier work [11]. The components of evolved gaseous mixtures were monitored using FTIR gas analyser (Interspectrum). The Ranger-AIP Gas cell S/N 23790 (Reflex Analytical Co.) with 8.8 meter 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 scans were made for the spectra. The evolution profiles of gases obtained as derivatives of the characteristic peak intensity (dI/dt) or the peak area (dS/dt), integrated above the FTIR spectrum baseline, were applied to characterize the evolution dynamics.

The simultaneous TG/DTA/EGA-MS measurements were performed in an apparatus consisting of an STD 2960 Simultaneous DTA/TGA (TA Instruments, USA) thermal analyzer and a Thermostar GSD 300 (Balzers Instruments) 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. First, mass spectra of the evolved gaseous mixtures were continuously scanned and collected between m/z=1–200 (SCAN-mode), then 64 mass/charge numbers were selected and their ion currents were monitored in multiple ion detection (MID) mode with the measuring time of 0.5 s for each channel. Samples with an initial mass of 38.82 mg (Ti-1) and 33.52 mg (Ti-2) were used for the experiments. The measurements were carried out in a dynamic air atmosphere using the gas flow rate of 130 mL min^{-1} and the heating rate of 10°C min^{-1}.

The evolved gases were identified on the basis of their FTIR and MS reference spectra available on world wide web in the public domain spectrum libraries of NIST and SDBS [14, 15].

Results and discussion

Characterization of xerogels, Ti-1 and Ti-2

FTIR spectrum of the xerogel synthesised at the TTIP:acacH molar ratio of 1:1 (Ti-1) was presented and discussed in our previous work [11]. From a qualitative point of view, the FTIR spectra of the xerogels, Ti-1 and Ti-2, are similar and close to the spectra of reddish-brown particles $TiO(acac)_2$ (titanium(IV) oxide acetylacetonate; Aldrich-Sigma Product No. 3300833, Lot No. 00408BE). According to the elemental analysis, carbon content was found to be 18.91 and 27.76 mass% and that of hydrogen 3.24 and 3.35 mass% in Ti-1 and Ti-2, respectively. According to the XRD profiles, the samples are amorphous, but Ti-1 shows a broad peak centred at ca. $2\theta=6°$, which could be interpreted as indicating a ca. d=14.6 Å average pore-size with a certain pore-size distribution [16].

Thermal analysis

Figure 1 shows the thermal behaviour of Ti-1 by depicting the TG, DTG and DTA curves. Six mass loss steps could be detected according to the DTG curve. The first mass loss step between 30–151°C is an endothermic reaction with a mass loss of 9.5 %. The fol-

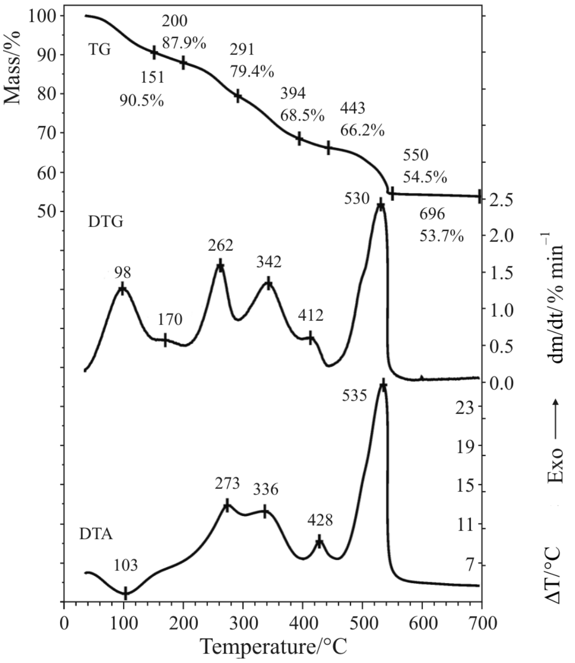

Fig. 1 Simultaneous TG, DTG and DTA curves of Ti-1 (TTIP:acac=1:1). Flowing air: 130 mL min^{-1}, heating rate: 10°C min^{-1}. Sample mass: 38.82 mg

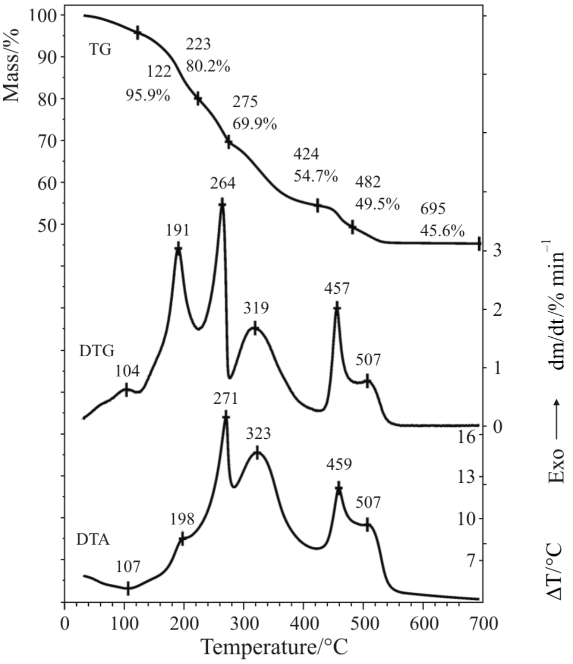

Fig. 2 Simultaneous TG, DTG and DTA curves of Ti-2 (TTIP:acac =1:2). Flowing air: 130 mL min^{-1}, heating rate: 10°C min^{-1}. Sample mass: 33.52 mg

lowing DTG maxima (2, 3, 4, 5, 6) at 170, 262, 342, 412, 530°C, respectively, are exothermic reactions according to DTA. The step 2, however, is very small as the observed mass loss is below 3%. In case of Ti-2 with its higher acac content, the second step is a significant one as seen in all TA curves (cf. Figs 2, 4 and 6). Decomposition of xerogel is practically completed by 540°C. According to the TG curve, the total mass loss in the temperature interval of 30–700 °C is 46.3%. When the heating rate of 5°C min^{-1} was used, the total mass loss in the temperature interval of 30–900°C was slightly less or 43.8% [11].

For Ti-2 six distinct mass loss steps could be detected according to the DTG curve (Fig. 2). The first mass loss step between 30–122°C is an endothermic reaction with a mass loss of 4.1%. The following DTG maxima (2, 3, 4, 5, 6) at 191, 264, 319, 457 and 507°C, respectively, are exothermic reactions according to DTA. The TG curve shows then an insignificant mass drop at temperatures above 500°C. The total mass loss in the temperature region of 30–700°C is 54.4%. The thermal behaviour of various sample charges of Ti-2 is not very reproducible as for another charge a mass loss of 60.0% was observed. In the case of Ti-1, the samples showed some signs of aging within a period of half a year.

According to XRD, the solid residues obtained at 700°C in air contain rutile (PDF 00-21-1272) and anatase (PDF 00-21-1276) in an approximate ratio of 72:28 and 26:74 for Ti-1 and Ti-2, respectively. The calculation is based on RIR (reference intensity ratio) data of the reference patterns [17].

Based on the final residual masses, the molar masses of Ti-1 and Ti-2 are between 143-149 and 175-200 g mol^{-1}, respectively. Thus, as expected, the amount of the organic matter in Ti-2 is significantly larger than in Ti-1. Based on the IR spectra comparisons and taking into account the initial mass and carbon content of the xerogel as well as the extent of the first mass loss (quantified only to the water release) and the final mass in xerogel heat treatments, the following approximate nominal compositions are suggested: $TiO_{1.325}(OH)_{0.90}(acac)_{0.45}\cdot 0.78H_2O$ for Ti-1, and $TiO_{0.8}(OH)_{1.6}(acac)_{0.8}\cdot 0.4H_2O$ for Ti-2. The other possible organic moieties are considered to be only minor ones, and therefore omitted from the formulas.

The first decomposition step for both Ti-1 and Ti-2 consists of the evolution of water as confirmed by both MS (cf. chapter on Evolved gas analysis) and EGA-FTIR [11]. Main difference in the decomposition behaviour of the xerogels studied, Ti-1 and Ti-2, is observed in the first three decomposition steps (30–291°C for Ti-1 and 30–275°C for Ti-2), showing quite different total mass losses of 20.6 and 30.1%, respectively. The mass losses in the following decomposition steps 4–6 (in the temperature region from about 300 up to 700°C) resemble each other (Figs 1 and 2), giving 25.7% for Ti-1 and 24.3% for Ti-2. The decompositions of Ti-1 and Ti-2 are completed at almost same temperatures, *viz.* 550 and 540°C, respectively.

Evolved gas analysis by FTIR

TG/DTG/DTA curves coupled with simultaneous EGA-FTIR measurements were recorded between 30 and 700°C while the FTIR spectra were recorded in the wavenumber range of 4000–400 cm^{-1}. The evolution of adsorbed or weakly bound H_2O was eliminated by pre-heating the sample in air up to 120°C. Hence the spectra became clearer and the absorption peaks better defined. In order to identify evolved gases, the measured spectra were analysed by taking the reference spectra from the database (NIST) and comparing them to the evolved gas spectra at different temperatures (Figure not shown).

Figures 3 and 4 show the derivative gas evolution profiles (Ti-1 and Ti-2, respectively), obtained as derivatives of the peak intensities (dI/dt) or the peak areas (dS/dt), and integrated above the FTIR spectrum baseline. The temperatures for gas evolution and temperatures of the evolution maxima ($dI/dt=0$) are marked in the figures. For CO_2, the peak areas in the region of 2215–2405 cm^{-1} were used for the calculations. The non-overlapping C=O vibrations were used to identify the evolved gases: acetic acid (1773 cm^{-1}), acetone (1746 cm^{-1}), and acetylacetone (1623 cm^{-1}). Using this procedure, all absorptions of the measured spectra could be matched with the gas spectra from the database, except for the absorption band recorded in the region 1027–1100 cm^{-1} (with the maximum at 1060 cm^{-1}) which does not match with any of the above-mentioned gas spectra.

In the case of Ti-1 (Fig. 3), the main evolved gases in the temperature interval of 100–310°C are acetone and acetic acid which could most probably be the decomposition products of metal-acetylacetonate [9]. The intensities of the characteristic peaks of acetone and acetic acid reach their maxima at 290–310°C, being typical for the decomposition step 3. Evolution of CO_2 starts at 160°C and its evolution maxima are located at 365, 390, 435 and 540°C.

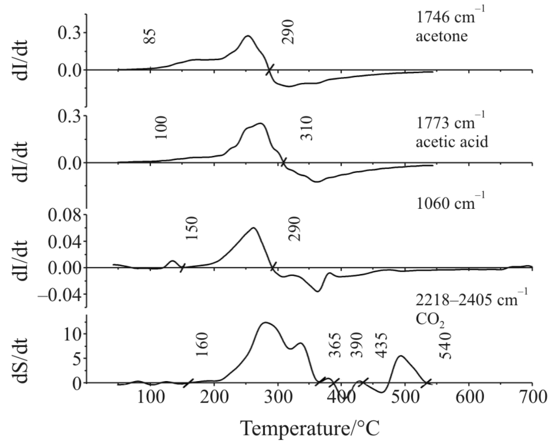

Fig. 3 Derivative evolution profiles of gases as determined by EGA-FTIR for Ti-1 (1:1). Flowing air: 130 mL min^{-1}, heating rate: 10°C min^{-1}. Sample mass: 33.4 mg. Ti-1 sample was pre-heated in air up to 120°C. The starting and maximum temperatures ($dI/dt=0$) of gas evolution are also given

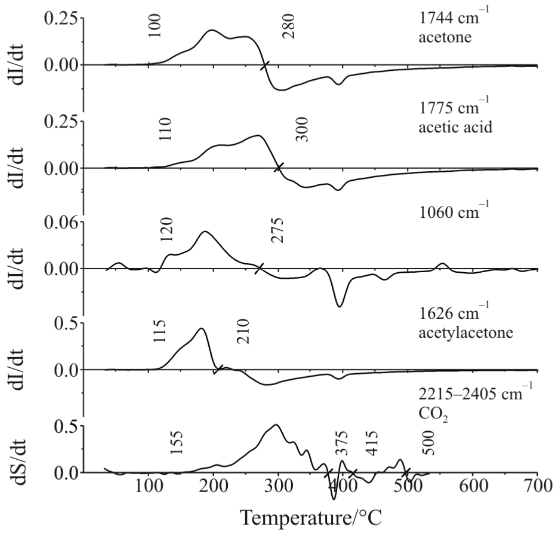

Fig. 4 Derivative evolution profiles of gases as determined by EGA-FTIR for Ti-2 (1:2).Flowing air: 130 mL min^{-1}, heating rate: 10°C min^{-1}. Sample mass: 37.3 mg. Ti-2 sample was pre-heated in air up to 120°C. The starting and maximum temperatures ($dI/dt=0$) of gas evolution are also given

It should be mentioned that no evolution of isopropylacetate was observed in the current experiment using the heating rate of 10°C min^{-1}, though the evolution of isopropylacetate was proposed as a decomposition product of the same complex in our previous work where the heating rate of 5°C min^{-1} was used [11].

In the case of Ti-2 (Fig. 4), the initially evolved gas is acetylacetone, reaching its maxima at 210°C and being characteristic for the decomposition step 2. Acetone and acetic acid with their evolution maxima at 280 and 300°C, respectively, are showing only about half of the evaporation intensity of acetylacetone. Evolution of CO_2 starts at 155°C and it is continuously evolving also in the next decomposition steps showing maxima at 375, 415 and 500°C.

Unfortunately, EGA-FTIR does not unambiguously distinguish evolved gases due to the possible overlapping of their characteristic vibrations. Therefore, the evolved gases were characterized also by MS analyses.

Evolved gas analysis by MS

Preliminary scanning of the spectra of evolved gas mixtures up to $m/z=200$ confirmed that volatile Ti-acetylacetonate species are not at all present during the thermal decomposition of the xerogel samples.

Figures 5 and 6 show the evolution profiles of evolved gaseous species from the xerogels Ti-1 and Ti-2, respectively. The decomposition starts with the evolution of H_2O, having a well-shaped maximum at 115°C irrespective of the sample. Hence, the endothermic peaks at 98 and 104°C in the DTG curves (Figs 2 and 3) of Ti-1 and Ti-2, respectively, can be assigned as belonging to H_2O. According to the TG-MS analysis, the main evolution of organic molecular species occurs at temperatures above 100°C and is characteristic for the decomposition steps 2 and 3 in the TG curves (Figs 1 and 2). Partial oxidation of the organic constituents also takes place in each decomposition step from 3 to 6, which is indicated by their exothermic heat effects and by the more or less continuous formation of H_2O (m/z=18) and CO_2 (m/z=44) as oxidation products in these steps (Figs 5 and 6).

In the case of Ti-1, evolution of acetone (m/z=58, CH_3COCH_3) starts around 115°C and shows a constant level between 195 and 220°C. The evolution continues in the third decomposition step with its maximum at 260°C. The evolution of acetic acid (m/z=60, CH_3COOH), observed in the temperature range of 150–350°C, is characteristic for the third decomposition step. Evolution of acetone and acetic acid was also detected by EGA-FTIR measurements as discussed above. In addition, gaseous species with m/z=72, 74, 75, showing similar evolution profiles, were observed (presented by m/z=74 in Fig. 5). It could be speculated that the methoxyethoxy group is present in the structure of the precursor as reported for the Zn-alkoxides in 2-methoxyethanol [12, 18]. The gaseous species with intense ion fragment of m/z=74 could belong to 2-methoxy-acetaldehyde (Figs 5 and 6). Nevertheless several other $C_3H_6O_2$ compounds with the molecular ion fragment of m/z=74, such as propanoic acid, ethyl formate, methyl acetate or 3-hydroxypropane aldehyde, can not be excluded.

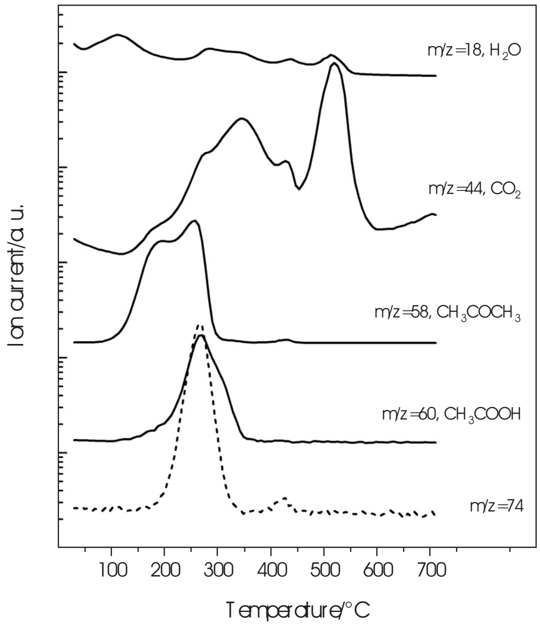

Fig. 5 Evolution profiles of gaseous species as monitored by TG/DTA-EGA-MS for the sample Ti-1 (1:1). Flowing air: 130 mL min^{-1}, heating rate: 10°C min^{-1}; sample mass: 38.82 mg

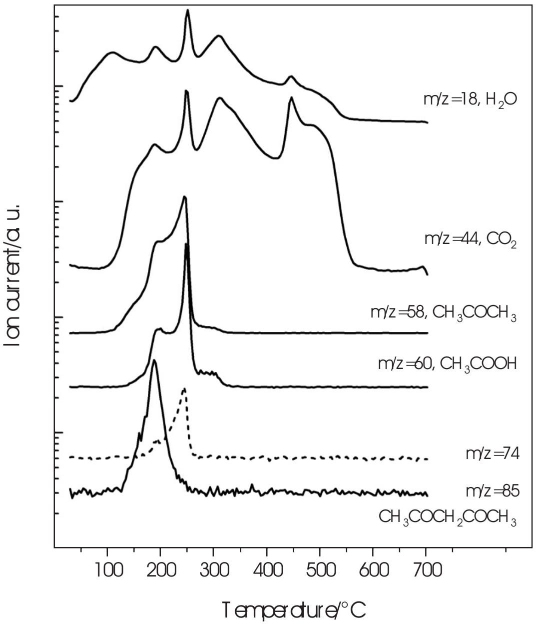

Fig. 6 Evolution profiles of gaseous species as monitored by TG/DTA-EGA -MS for the Ti-2 (1:2). Flowing air: 130 mL min^{-1}, heating rate: 10°C min^{-1}; sample mass: 33.52 mg

We did not observe the evolution of either alcohols (2-propanol, or 2-methoxyethanol) or propene ($CH_3CH=CH_2$) either by MS or EGA-FTIR. However, Campostrini *et al.* have recently reported the evolution of 2-propanol and propene from the Ti(IV) isopropoxide complexes with formic, acetic or oxalic acids at temperatures up to 300°C using combined TG-GC-MS [6–8, 19]. In case of gels modified by oxalic acid, the isopropanol and propene evolve already at 125°C [7]. This may indicate that our boiling step at 130°C could be effective enough to completely eliminate the isopropoxide moieties.

In the case of Ti-2, the main gaseous species released in the second step is acetylacetone (main characteristic fragments are m/z=85 and 100, *viz.* $CH_3COCH_2COCH_3$) with the maximum at 195°C (presented by m/z=85 in Fig. 6). Simultaneously, a partial evolution of acetone and acetic acid appears to begin, indicated by ion fragments m/z=58 and m/z=60, respectively. The maximum evolution of acetone and acetic acid was observed in step 3, together with that of *m*/*z*=74 which occurred at 265°C (Fig. 6). Similar products, *viz.* acetylacetone, acetone, acetic acid, CO_2 and CO were observed by high resolution MS during thermal decomposition of Cu(II)-acetylacetonate [9]. Altogether, the intense evolution of acetylacetone from the sample Ti-2 (TTIP:acac=1:2) in the decomposition step 2 is the main difference compared to Ti-1 (TTIP:acac=1:1), where no release of acetylacetone was observed. The evolution of entire acetylacetone molecules in the case of Ti-2 might be explained with either their at least partial entrapment in the pores of the xerogel formed, or with an easy proton migration from OH to acetylacetonate groups which is facilitated in the Ti-2 sample by the higher concentrations of both OH and acac moieties than those present in the Ti-1 sample. The proton migration can also be considered as a condensation reaction in spatially favoured cases between the OH and acac moieties as formulated by the following equation:

$$\equiv \text{Ti–acac} + \equiv \text{Ti–OH} \rightarrow \equiv \text{Ti–O–Ti} \equiv + \text{acacH}$$

In general, our MS data confirm the results obtained by EGA-FTIR but show more explicit evolution profiles of H_2O and CO_2. In addition, a gaseous species with *m*/*z*=74 was observed to evolve from both precursors but it could not be unambiguously identified. Additional solid state MAS-NMR and pyrolysis GC-MS investigations might provide more information and knowledge needed to further characterize the precursor xerogels [20] and their thermal decomposition [19].

Conclusions

Thermal degradation of the xerogel samples Ti-1 and Ti-2 in the temperature range of 30–700°C consists of 6 mass loss steps irrespective of the xerogel. According to the TG curve, the total mass loss of Ti-1 and Ti-2 in the temperature interval of 30–700°C is 46.3 and 54.4%, respectively. The xerogels studied release only water up to 120°C. The further decomposition steps are exothermic and include the evolution of CO_2 and H_2O, arising from burning of organic residues up to 550°C.

In the temperature region of 120–320°C, the main released gases were acetone, acetic acid released from both precursors, and acetylacetone evolved from Ti-2 only, as shown by both EGA-FTIR and EGA-MS. In addition, according to EGA-MS, the gaseous species with *m*/*z*=74 was evolved from both xerogels at temperatures above 200°C. To identify all gaseous species released as well as to explain the evolution of acetylacetone from Ti-2 only would require a deeper structural characterisation of the precursor xerogels.

Considering also the previous TG/DTG/DTA data on Ti-1 [11], it is now possible to compare the effect of heating rate as well as the composition of xerogels. As expected, the lower heating rate (5 *vs.* 10°C min^{-1}) moves the starting of decomposition towards lower temperatures by some tens of degrees. The weak DTG/DTA peak of Ti-1 at 412/428°C (present work) appears to be absent in the data for Ti-1 recorded at 5°C min^{-1} in an other apparatus [11]. On the other hand, the previous Ti-1 data [11] exhibit a weak exothermic peak at 763–765°C which is beyond the present temperature range and could thus not be confirmed. The increased content of organic matter (acac) in the case of Ti-2 is visible as an additional, strong DTG peak at 191°C as well as in the EGA patterns where the maximum acacH evolution at 195°C coincides with this temperature.

Our results form another example that chemical modification of the precursor [10] and experimental conditions greatly influence the mechanism of a sol–gel process.

Acknowledgements

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