

# Evolved gas analysis of amorphous precursors for S-doped TiO<sub>2</sub> by TG-FTIR and TG/DTA-MS

## Part 3. Candidate from thiourea and Ti(IV)-ethoxide

János Madarász · Ana Brăileanu · Maria Crișan ·  
Malina Răileanu · György Pokol

ICTAC2008 Conference  
© Akadémiai Kiadó, Budapest, Hungary 2009

**Abstract** Thermal decomposition of an amorphous precursor for S-doped titania (TiO<sub>2</sub>) nanopowders, prepared by controlled sol–gel hydrolysis–condensation of titanium(IV) tetraethoxide and thiourea in aqueous ethanol, has been studied up to 800 °C in flowing air. Simultaneous thermogravimetric and differential thermal analysis coupled online with quadrupole mass spectrometer (TG/DTA-MS) and FTIR spectrometric gas cell (TG-FTIR) have been applied for analysis of released gases (EGA) and their evolution dynamics in order to explore and simulate thermal annealing processes of fabrication techniques of the aimed S:TiO<sub>2</sub> photocatalysts with photocatalytic activities under visible light. The precursor sample prepared with thiourea, released first water endothermically from room temperature to 190 °C, carbonyl sulfide (COS) from 120 to 240 °C in two stages, ammonia (NH<sub>3</sub>) from 170 to 350 °C in three steps, and organic matter (probably ether and ethylene) between 140 and 230 °C. The evolution of CO<sub>2</sub>, H<sub>2</sub>O and SO<sub>2</sub>, as oxidation products, occurs between 180 and 240 °C, accompanied by exothermic DTA peaks at 190 and 235 °C. Some small mass gain occurs before the following exothermic heat effect at 500 °C, which is probably due to the simultaneous burning out of residual carbonaceous and sulphureous species, and transformation of amorphous titania into anatase. The oxidative process is

accompanied by evolution of CO<sub>2</sub> and SO<sub>2</sub>. Anatase, which formed also in the exothermic peak at 500 °C, mainly keeps its structure, since only 10% of rutile formation is detected below or at 800 °C by XRD. Meanwhile, from 500 °C, a final burning off organics is also indicated by continuous CO<sub>2</sub> evolution and small exothermic effects.

**Keywords** Anatase · Evolved gas analysis · FTIR-spectroscopic gas cell · Mass spectrometry · Simultaneous thermogravimetry and differential thermal analysis · Thiourea · Titania precursor · Titanium(IV)-ethoxide

## Introduction

Extension of photocatalytic activity of titanium dioxide photocatalysts beyond UV light toward visible light is of growing importance in the field of photodegradation of pollutants in water and atmosphere [1–15]. Recently, preparation of several specifically doped or modified titania substrates, mostly various S-(sulfur-), C-(carbon-), and N-(nitrogen-) doped titania with anatase structure were reported to absorb visible light [1–15]. In case of S-doping, the sulfur was detected in form of sulfide (S<sup>2-</sup>) [3, 8], or S(VI) [4], or tetravalent S(IV) substituting Ti<sup>4+</sup> cations [4–6] by XPS. Nevertheless, in a latter case, S<sup>4+</sup> can be attributed not only to the bulk sulfurous content, but rather to surface adsorbed SO<sub>2</sub> species [11].

Thiourea (thiocarbamide, SC(NH<sub>2</sub>)<sub>2</sub>) seems to be a very promising sulfur-source for S-doped TiO<sub>2</sub>, applying with various Ti-compounds as titania source, such as TiO<sub>2</sub> (anatase and rutile) modifications [1, 4, 6, 12, 15] obtained by calcination below 600 °C, or Ti(III) and Ti(IV)-chlorides by hydrothermal treatment at 190 °C [13] or a sol–gel method at

J. Madarász (✉) · G. Pokol  
Department of Inorganic and Analytical Chemistry, Budapest  
University of Technology and Economics, Szt. Gellért tér 4,  
Budapest 1521, Hungary  
e-mail: madarasz@mail.bme.hu

A. Brăileanu · M. Crișan · M. Răileanu  
Roumanian Academy, Institute of Physical Chemistry Ilie  
Murgulescu, 202 Splaiul Independenței, Bucharest 060021,  
Romania

100 °C for 10 h [14], respectively, or various Ti(IV)-alkoxides by sol–gel processes followed by thermal annealing of solid xerogel precursors in the temperature range of 400–700 °C [1, 4–9]. Anyhow, Sakthivel et al. [10] obtained N-doped TiO<sub>2</sub> when they reproduced the preparation route of Ref. [4], which used alcohol as solvent with Ti(IV)-tetraisopropoxide and thiourea. They used water instead of alcohol and obtained the desired S-doped sample [10]. Simultaneously S- and C-doped precursors were also prepared by combined application of thiourea and urea [7, 11].

The thermal annealing process of precursor mixtures of titania xerogels containing thiourea can be studied by methods of thermal analysis, especially with simultaneous thermogravimetry (TG) and differential thermal analysis (DTA) [11, 16]. To get a deeper insight into the thermal processes of decompositions, various methods of evolved gas analysis (EGA) of the precursors are also advantageous [16–30]. As spray pyrolysis precursors, various thiourea–metal salt complexes of Cd, Zn, Sn(II) and pure thiourea itself have recently been studied in situ by online coupled TG-DTA-MS and TG-FTIR spectroscopic gas cell system [21–26]. Thermal decomposition of various precursor titania sols for fabrication of porous and smooth films and layers of dye-sensitized solar cells are also studied by us with EGA methods [29–31].

As a part of our ongoing thermal studies on amorphous precursor materials for pure and S-doped TiO<sub>2</sub> sol–gel nanopowders prepared by controlled hydrolysis-condensation of various titanium alkoxides (tetraethyl-, tetraisopropyl- and tetrabutyl-orthotitanate) in mixture with 5% thiourea [16], we have carried out now evolved gas analysis (EGA) on samples obtained with Ti(IV)-ethoxide, by both on-line coupled TG-FTIR gas cell and TG/DTA-MS equipments, complementing our former results obtained in static air (self-generated) atmosphere [16, 32]. Similarly to the case of Ti(IV)-isopropoxide [33] and Ti(IV)-*n*-butoxide [34] we have identified and monitored gaseous species thermally evolved in flowing air atmosphere, and also aimed identification of S- and other type doping species incorporated into the precursors and their titania powders for photocatalytic activity under visible light. Both evolved gas analyses were done in air atmosphere, in order to observe relatively low amount of strongly retained doping elements (S, C, and N) in form of oxidized inorganic gases released at high temperatures.

## Experimental

### Samples and methods

Precursor xerogel samples **1** (EtO–TiO<sub>2</sub>) and **2** (EtO–tu–TiO<sub>2</sub>) for TiO<sub>2</sub> and S:TiO<sub>2</sub> were prepared following the

procedure given in Refs. [16, 32], synthesized starting from Ti(IV)-tetraethoxide without and with thiourea (5% mass ratio to Ti(OEt)<sub>4</sub>), respectively, in aqueous ethanol at room temperature, while the intermediate sols were concentrated at 80 °C.

FTIR spectra of samples **1** (EtO–TiO<sub>2</sub>) and **2** (EtO–tu–TiO<sub>2</sub>) were recorded with an Excalibur Series FTS 3000 (Biorad) FTIR spectrophotometer in KBr between 700 and 4000 cm<sup>-1</sup>, while the XRD patterns of the samples and their decomposition products (TiO<sub>2</sub> and S:TiO<sub>2</sub>) obtained at various temperatures in the thermal balances were recorded on X'pert Pro MPD (PANalytical, The Netherlands) X-ray diffractometer using CuK<sub>α</sub> radiation with Ni filter and X'celerator detector.

The CH-elemental analysis with an Vario EL III, (Elementar Analysensysteme GmbH, Germany) CHN-O Analyser showed the following percentage of carbon, hydrogen, and nitrogen: C% 0.36; H% 2.18, N% 0 for Sample **1** (EtO–TiO<sub>2</sub>), and C% 3.90; H% 3.30, N% 4.90 for Sample **2** (EtO–tu–TiO<sub>2</sub>).

### In situ 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), with a heating rate of 10 °C min<sup>-1</sup>, an air flow rate of 130 mL/min, sample masse between 11 and 28 mg, and open Pt crucible was used. The mixture of gaseous species could reach a ThermoStar GDS 200 (Balzers Instruments) quadrupole mass spectrometer equipped with Chaneltron detector, 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 Multiple Ion Detection mode (MID) monitoring 64 selected channels ranging mostly between  $m/z$  12 and 78. Measuring time was ca. 0.5 s for one channel, resulting in time of measuring cycles of ca. 30 s.

### In situ EGA by coupled TG-FTIR

A TGA 2050 Thermogravimetric Analyzer (TA Instruments, USA) with a heating rate of 10 °C min<sup>-1</sup>, with air flow rate of 120 mL/min, (and an extra 10 mL/min air as a balance purge) and sample masses in the 35–41 mg range in open Pt crucible were used. Gaseous species evolved from the sample 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 ( $l = 90$  cm,  $d_m = 2$  mm) kept at  $T = 180$  °C. FTIR spectra (550–4000 cm<sup>-1</sup>) were collected 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.

## FTIR spectroscopic and mass spectrometric identification of various gaseous species

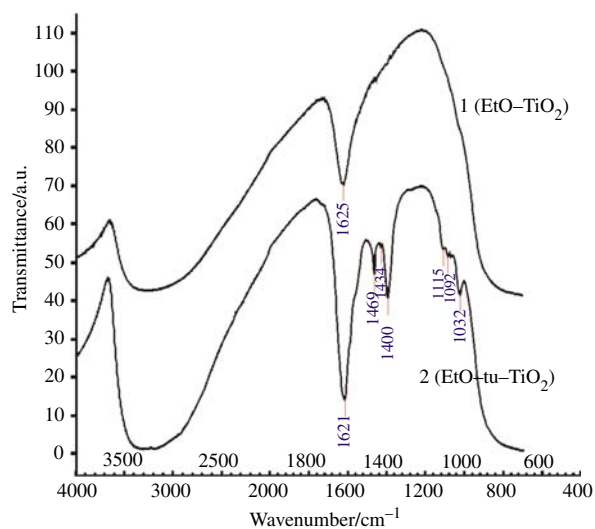
The components of released gaseous mixtures were monitored and identified mostly on the basis of their FTIR and MS reference spectra available on worldwide web in the public domain spectral libraries [35, 36] or collected from the original literature [26].

## Results and discussion

FTIR characterization of amorphous precursor samples **1** (EtO–TiO<sub>2</sub>) and **2** (EtO–tu–TiO<sub>2</sub>) for TiO<sub>2</sub> and S:TiO<sub>2</sub>, respectively

FTIR spectra of samples **1** (EtO–TiO<sub>2</sub>) and **2** (EtO–tu–TiO<sub>2</sub>) are shown in Fig. 1. Sample **1** (EtO–TiO<sub>2</sub>) shows almost only vibration of adsorbed water. For a reference spectra of fully hydrolyzed titania xerogel prepared from Ti(OiPr)<sub>4</sub> with SnCl<sub>2</sub> catalyst see Ref. [37].

The spectrum of sample **2** (EtO–tu–TiO<sub>2</sub>) resembles to that of n-butoxide (nBuO–tu) samples similarly prepared with thiourea [34]. Bands at 1469 cm<sup>-1</sup> and 1000–1250 cm<sup>-1</sup> show presence of alkoxy (ethoxy) groups, while the spectrum of sample **2** (EtO–tu–TiO<sub>2</sub>) presents an additional vibration band at 1400 cm<sup>-1</sup> close to those of isopropoxy (iPrO–tu, [33]) and n-butoxy (nBuO–tu, [34]) samples, similarly prepared with thiourea (1399 and 1398 cm<sup>-1</sup>, respectively), originating from the incorporated thiourea. Anyway, it is different from the bands of



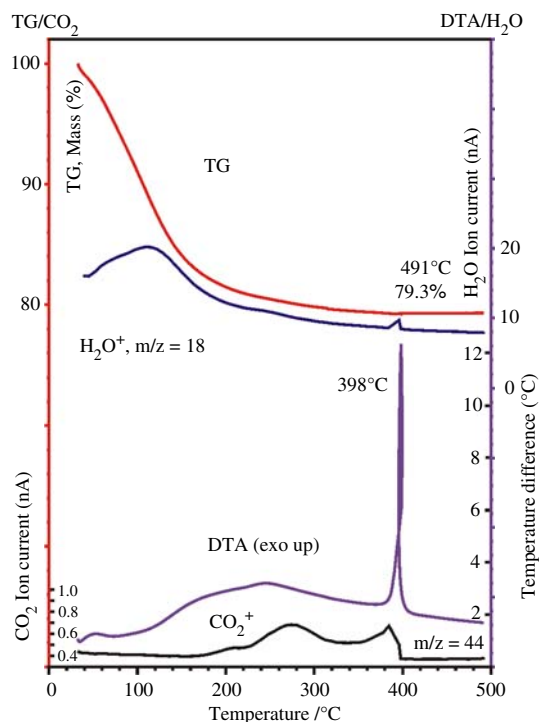
**Fig. 1** FTIR(KBr) spectra of sample **1** (EtO–TiO<sub>2</sub>) (upper curve) and sample **2** (EtO–tu–TiO<sub>2</sub>) (bottom curve)

pure thiourea (1618, 1473, 1414, 1206, and 1083 cm<sup>-1</sup>) [33, 34], and from those published in spectra of Ti–thiourea residues [10, 11, 38].

Thermal behavior of sample **1** (EtO–TiO<sub>2</sub>) precursor for TiO<sub>2</sub> in the online coupled simultaneous TG/DTA–MS apparatus

For sake of better comparison, simultaneous thermogravimetric (TG), differential thermal analytical (DTA), and mass spectroscopic curves (m/z 18 and m/z 44) of sulfur-free sample **1** (EtO–TiO<sub>2</sub>) are shown in Fig. 2. The decomposition in air shows the evolution of mainly water up to 160 °C, process which is slightly endothermic. Between 160 and 400 °C, the evolution of mainly carbon dioxide takes place, which becomes highly exothermic at 400 °C also because of overlapping crystallization of amorphous titania into anatase.

Toshikazu et al. [39, 40] reported recently evolved gases from titania gel films which had been prepared by HCl catalyzed hydrolysis of Ti(IV)–ethoxide, in Temperature Programmed Desorption vacuum mass spectroscopic apparatus. They have observed water (m/z 18) evolution at around 100 °C (large peak) and 210 °C (small peak), while



**Fig. 2** Simultaneous TG/DTA and mass spectroscopic curves (m/z 18 and m/z 44) of sample **1** (EtO–TiO<sub>2</sub>), as measured in situ by the online coupled TG/DTA–MS system in Multiple Ion Detection mode (Air flow 130 mL/min, heating rate 10 °C/min, initial mass 11.90 mg)

ion fragments from the ethanolato ligands are detected at around 210 °C (large peak) and at around 335 °C (small peak) [39, 40]. In our case, in air, the organic vapors released from **1** (EtO–TiO<sub>2</sub>) are directly oxidized to CO<sub>2</sub> and water.

Evolution of gaseous species from samples **2** (EtO–tu–TiO<sub>2</sub>) precursor for S:TiO<sub>2</sub> measured in situ by TG/DTA-EGA-MS system and TG-FTIR spectrometric gas cell

The simultaneous thermogravimetric (TG), derivative thermogravimetric (DTG), differential scanning calorimetric (DTA) curves, and a mass spectroscopic curve (*m/z* 64, SO<sub>2</sub>) of sample **2** (EtO–tu–TiO<sub>2</sub>) are shown in Fig. 3. All the evolution patterns of individual gaseous products of decomposing sample **2** (EtO–tu–TiO<sub>2</sub>), as identified and monitored by TG/DTA-EGA-MS and TG-EGA-FTIR-gas cell measurement system, are shown in Figs. 4 and 5, respectively.

TG curve of **2** (EtO–tu–TiO<sub>2</sub>) exhibits at least seven mass change stages up to 800 °C (Fig. 3) marked according to the DTG curve minima. The initial mass loss is associated with endothermic release of water starting from

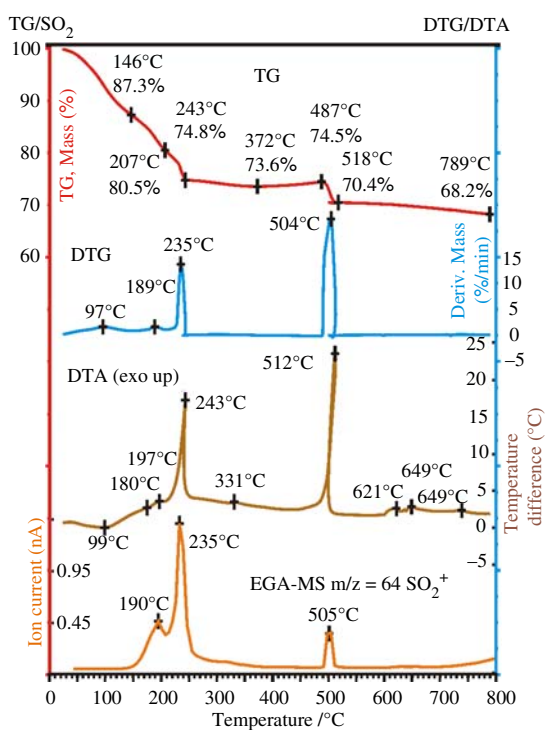
room temperature up to 146 °C, centered at 99 °C, as in case of **1** (EtO–TiO<sub>2</sub>). The evolution of water is confirmed by both EGA methods, although slight release of some organics, most probably ethanol, can not be excluded according to the spectra of the evolved gaseous mixtures.

The second decomposition stage (between 150 and 207 °C) is marked by a slight endothermic and a slight exothermic heat effect at 180 and 197 °C, respectively, which are close to melting point and starting oxidative degradation of pure thiourea [26]. Anyhow, starting from already 120 °C, an intense evolution of carbonyl sulfide (COS) occurs and reaches local maximal rates at about 160–170 °C, and oxidation products of carbonyl sulfide, such as sulfur dioxide (SO<sub>2</sub>) and CO<sub>2</sub> also starts and culminates first at 190 °C. At this temperature evolution of organic decomposition products and NH<sub>3</sub> also show a small peak.

Evolution of all these mentioned gaseous species is accelerated up in the third stage between 200 and 240 °C, (Figs. 4 and 5); the DTA curve presented a sharp exothermic heat effect at 235 °C. According to the EGA-MS evaluation small evolution of carbon disulfide and hydrogen chloride can not be excluded (Nishide et al. [39] observed evolution of HCl at about 210 °C). Anyway, the EGA-FTIR observation does not confirm the latter gases. Nevertheless, various organic species are evolved as part of degradation of both the organic residues and the incorporated thiourea derivatives of the titania. No doubt, three gases (COS, NH<sub>3</sub>, and SO<sub>2</sub>) can arise from thiourea or its derivatives by decomposition in air [26].

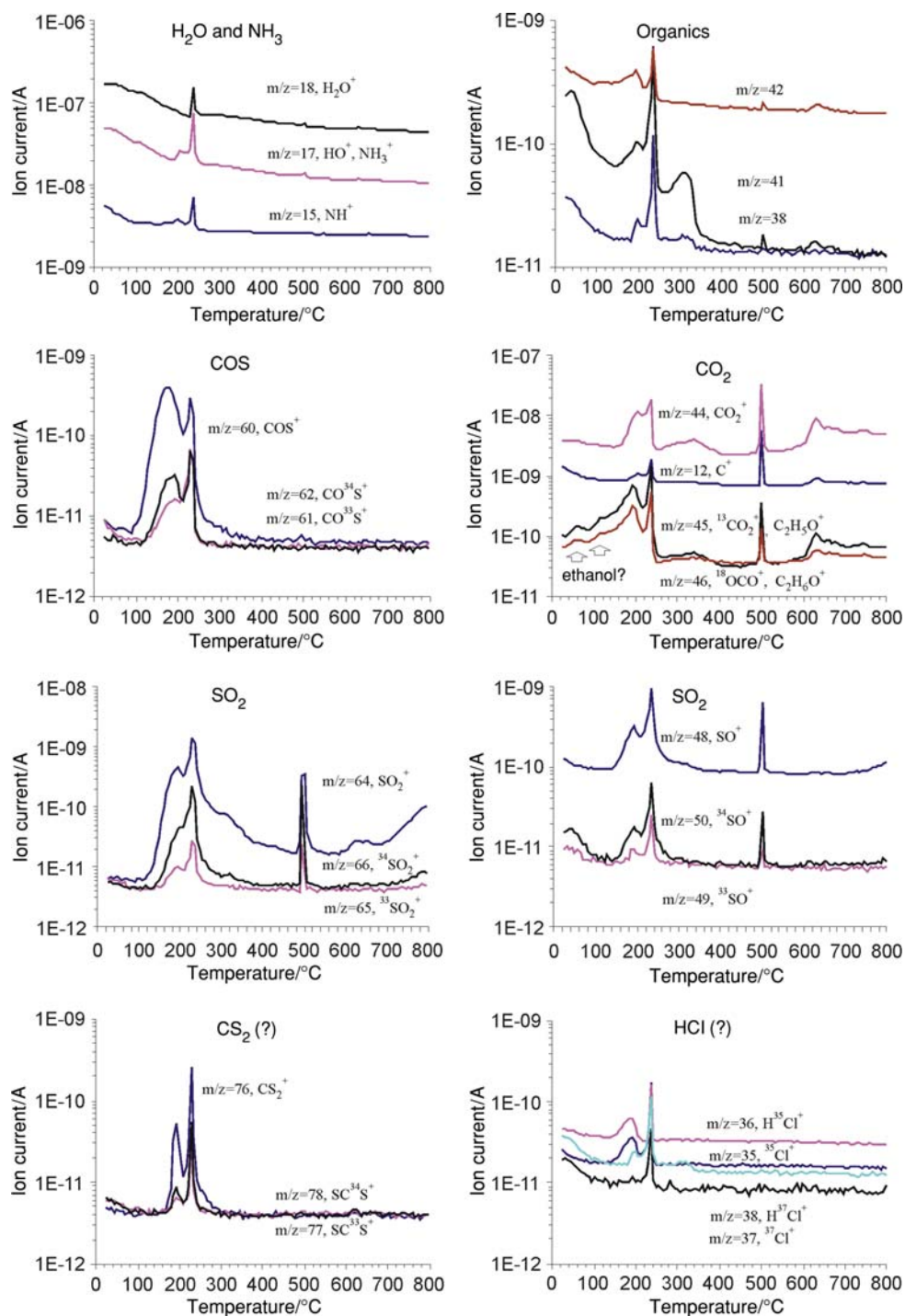
In the fourth stage, between 250 and 375 °C, elongated evolution of organics, and of their oxidation products CO<sub>2</sub> and water take place, indicated by a small exothermic heat effect at 330 °C (Fig. 3, DTA). In the fifth stage, between 375 and 490 °C, a slight mass gain occurs, most likely, as a result of oxygen uptake, which culminates at around 500 °C and bursts into a huge oxidation exothermic effect by burning out of solid organic residues into CO<sub>2</sub> and SO<sub>2</sub> (sixth step). The formation of crystalline anatase modification from the amorphous form takes also place in this step, accompanied by the exothermic crystallization heat. Despite the sharp heat effect, a continuous release of some organic residues in form of CO<sub>2</sub> above 500 °C (seventh stage), what has not stopped even at 800 °C and indicated also with small exothermic effects, has been still observed.

The identity and evolution course of the observed gaseous species by the parallel mass spectroscopic gas-evolution curves of various ion fragments of the above indicated decomposition products, (i.e. H<sub>2</sub>O, ammonia (NH<sub>3</sub>), carbonyl sulfide (COS), CO<sub>2</sub>, sulfur dioxide (SO<sub>2</sub>) and organic vapors) as released from sample **2** (EtO–tu–TiO<sub>2</sub>), are confirmed by the online coupled TG-EGA-FTIR system. The EGA-FTIR curve of water (neglecting its time



**Fig. 3** Simultaneous TG/DTG/DTA and mass spectroscopic curve (*m/z* 64) of sample **2** (EtO–tu–TiO<sub>2</sub>), as measured in situ by the online coupled TG/DTA-MS system in Multiple Ion Detection mode (Air flow 130 mL/min, heating rate 10 °C/min, initial mass 27.50 mg)

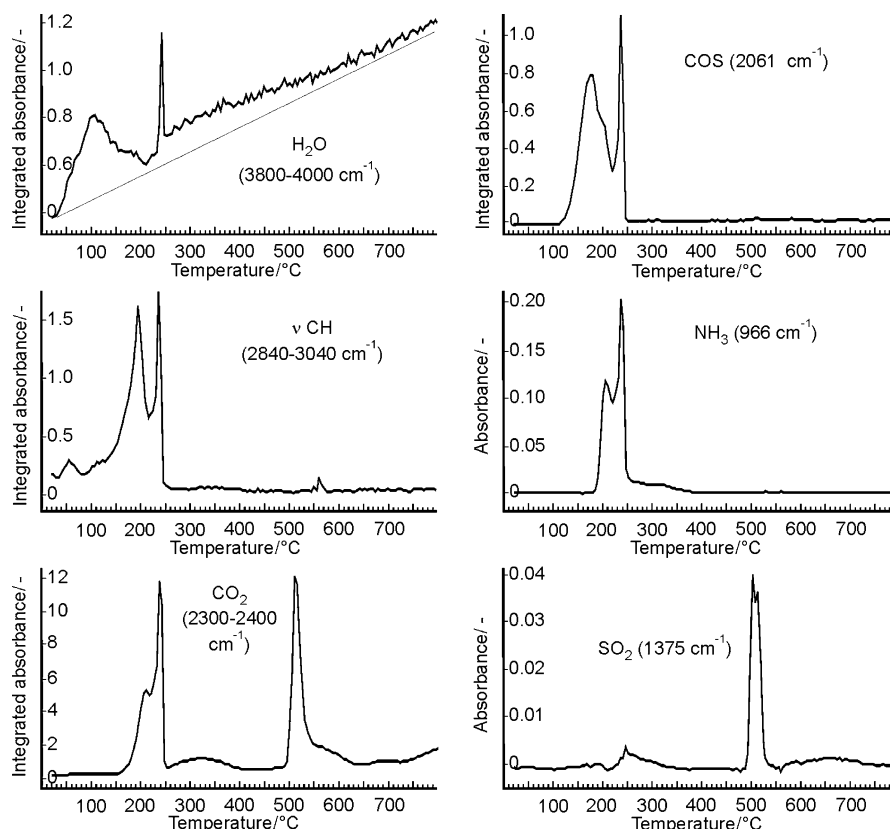
**Fig. 4** Mass spectroscopic gas-evolution curves represented by ion fragments of various gaseous species, such as H<sub>2</sub>O, ammonia (NH<sub>3</sub>), carbonyl sulfide (COS), CO<sub>2</sub>, sulfur dioxide (SO<sub>2</sub>) and organic vapors from sample **2** (EtO-tu-TiO<sub>2</sub>), measured by online coupled TG/DTA-EGA-MS system (air flow 130 mL/min, heating rate 10 °C/min, initial mass 27.50 mg)



drift) provided similar picture of H<sub>2</sub>O evolution as m/z 18 (H<sub>2</sub>O<sup>+</sup>) molecular ion gives. The EGA-FTIR curve of ammonia provides more detailed course than does the weak signals of m/z 15 (NH<sup>+</sup>). Note the EGA-MS m/z = 17 (OH<sup>+</sup> and NH<sub>3</sub><sup>+</sup>) curve shows a superposed picture of water and ammonia overlapping evolution. Both the isotopic distribution of S with mass number of 32, 33, and 34 in the EGA-MS spectra and the characteristic absorption

band in the EGA-FTIR spectra fully confirm the course of evolution of COS species from sample **2** (EtO-tu-TiO<sub>2</sub>) (Figs. 4 and 5). Isotopic ion fragments of SO<sub>2</sub> m/z 48, 50, and 49 (SO<sup>+</sup> from SO<sub>2</sub>) and the m/z 64, 66, and 65 (SO<sub>2</sub><sup>+</sup>) molecular ions indicates definite release of SO<sub>2</sub>, despite the fact that a parallel evolution of ammonia at around 200–250 °C seems to disturb technically somehow the EGA-FTIR detection of sulfur dioxide.

**Fig. 5** Evolution patterns of gaseous species, such as H<sub>2</sub>O, CO<sub>2</sub>, carbonyl sulfide (COS), ammonia (NH<sub>3</sub>), sulfur dioxide (SO<sub>2</sub>), and organic vapors from sample 2 (EtO–tu–TiO<sub>2</sub>) as observed in situ TG-EGA-FTIR measurement (Absorbance or integrated absorbance in the characteristic wavenumber regions, 10 °C/min heating rate, 130 mL/min air flow, initial mass 40.83 mg)



According to XRD analysis [41] of our residual S:TiO<sub>2</sub> samples, obtained in the thermal balances at 800 °C, contain mainly anatase, together with about 10% rutile TiO<sub>2</sub> only.

## Conclusions

Sample 1 (EtO–TiO<sub>2</sub>), precursor for TiO<sub>2</sub> contained so small amount of organic residues, which was not conclusively detected in the FTIR spectra, whilst sample 2 (EtO–tu–TiO<sub>2</sub>), precursor for S: TiO<sub>2</sub> contained ethoxy groups and thiourea residues according to its FTIR spectra. The presence of these residues is confirmed by the evolution of various gaseous species originating from the mentioned moieties. Definite release of carbonyl sulfide (COS) from 120 to 240 °C in two stages, of ammonia (NH<sub>3</sub>) from 170 to 370 °C in three steps has also been detected and monitored in situ by both EGA apparatus of TG-FTIR gas cell and TG/DTA-MS from sample 2 (EtO–tu–TiO<sub>2</sub>) prepared by thiourea addition. Furthermore, sulfur dioxide (SO<sub>2</sub>) originating from thiourea evolves in three steps centered at 190, 235, and 505 °C, accompanied by evolution of CO<sub>2</sub> and with more or less sharp exothermic heat effects in air, detected by both TG/DTA-MS and TG-FTIR methods. Evolution of CO<sub>2</sub> and SO<sub>2</sub> seems to be continued slowly even between 500 and 800 °C, still showing only less than

10% rutile modification of titania. Thus, dip coated thin film samples prepared at 500 °C [32] are the promising candidates for S:TiO<sub>2</sub> photocatalysts even under visible light.

**Acknowledgements** The authors thank Mrs. H. Medzihradzky for the elemental analysis measurements. The purchase of our new HT-XRD apparatus has been supported by the EU (GVOP-3.2.1.-2004-04-0224, KMA) and the Hungarian Government.

## References

- Bacsa R, Kiwi J, Ohno T, Albers P, Nadochenko V. Preparation, testing and characterization of doped TiO<sub>2</sub> active in the peroxidation of biomolecules under visible light. *J Phys Chem B*. 2005;109:5994–6003 (and references therein).
- Asahi R, Morikawa T, Ohwaki T, Aoki K, Taga Y. Visible-light photocatalysis in nitrogen-doped titanium oxides. *Science*. 2001;293:269–71.
- Umabayashi T, Yamaki T, Tanaka S, Asai K. Visible light-induced degradation of methylene blue on S-doped TiO<sub>2</sub>. *Chem Lett*. 2003;32:330–1.
- Ohno T, Mitsui T, Matsumura M. Photocatalytic activity of S-doped TiO<sub>2</sub> photocatalyst under visible light. *Chem Lett*. 2003;32:364–5.
- Ohno T, Akiyoshi M, Umabayashi T, Asai K, Mitsui T, Matsumura M. Preparation of S-doped TiO<sub>2</sub> photocatalysts and their photocatalytic activities under visible light. *Appl Catal A: Gen*. 2004;265:115–21.
- Ohno T. Preparation of visible light active S-doped TiO<sub>2</sub> photocatalysts and their photocatalytic activities. *Water Sci Technol*. 2004;49:159–63.

7. Tachikawa T, Toja S, Kawai K, Endo M, Fujitsuka M, Ohno T, et al. Photocatalytic oxidation reactivity of holes in the sulfur- and carbon-doped TiO<sub>2</sub> powders studied by time-resolved diffuse reflectance spectroscopy. *J Phys Chem.* 2004;108:19299–306.
8. Takeshita K, Yamakata A, Ishibashi T, Onishi H, Nishijima K, Ohno T. Transient IR absorption study of charge carriers photogenerated in sulfur-doped TiO<sub>2</sub>. *J Photochem Photobiol A: Chem.* 2006;177:269–75.
9. Ohno T, Miyamoto Z, Nishijima K, Kanemitsu H, Xueyuan F. Sensitization of photocatalytic activity of S- or N-doped TiO<sub>2</sub> particles by absorbing Fe<sup>3+</sup> cations. *Appl Catal A: Gen.* 2006;302:62–8.
10. Sakthivel S, Janczarek M, Kisch H. Visible light activity and photoelectrochemical properties of nitrogen-doped TiO<sub>2</sub>. *J Phys Chem B.* 2004;108:19384–7.
11. Sun H, Bai Y, Cheng Y, Jin W, Xu N. Preparation and characterization of visible-light-driven carbon–sulfur-codoped TiO<sub>2</sub> photocatalysts. *Ind Eng Chem Res.* 2006;45:4971–6.
12. Ohno T, Tsubota T, Toyofuku M, Inaba R. Photocatalytic activity of a TiO<sub>2</sub> photocatalyst doped with C<sup>4+</sup> and S<sup>4+</sup> ions having a rutile phase under visible light. *Catal Lett.* 2004;98:255–8.
13. Yin S, Ihara K, Aita Y, Komatsu M, Sato T. Visible-light induced photocatalytic activity of TiO<sub>2-x</sub>A<sub>y</sub> (A = N, S) prepared by precipitation route. *J Photochem Photobiol A: Chem.* 2006;179:105–14.
14. Xie Y, Zhao Q, Zhao XJ, Li J. Low-temperature preparation and characterization of N-doped and N–S-codoped TiO<sub>2</sub> by sol–gel route. *Catal Lett.* 2007;118:231–7.
15. Nishijima K, Kamai K, Murakami N, Tsubota T, Ohno T. Photocatalytic hydrogen or oxygen evolution from water over S- or N-doped TiO<sub>2</sub> under visible light. *Int J Photoenerg* 2008; Article ID 173943, 2008. doi: [10.1155/2008/173943](https://doi.org/10.1155/2008/173943).
16. Crişan M, Brăileanu A, Răileanu M, Crişan D, Teodorescu VS, Bîrjega R, et al. TiO<sub>2</sub>-based nanopowders obtained from different Ti-alkoxides. *J Therm Anal Calorim.* 2007;88:171–6.
17. Camprostrini R, Ischia M, Palmisano L. Pyrolysis study of sol–gel derived TiO<sub>2</sub> powders Part I. TiO<sub>2</sub>-anatase prepared by reacting titanium(IV) isopropoxide with formic acid. *J Therm Anal Calorim.* 2003;71:997–1009.
18. Camprostrini R, Ischia M, Palmisano L. Pyrolysis study of sol–gel derived TiO<sub>2</sub> powders Part I. TiO<sub>2</sub>-anatase prepared by reacting titanium(IV) isopropoxide with oxalic acid. *J Therm Anal Calorim.* 2003;71:1011–21 (and references therein).
19. Camprostrini R, Ischia M, Palmisano L. Pyrolysis study of sol–gel derived TiO<sub>2</sub> powders Part I. TiO<sub>2</sub>-anatase prepared by reacting titanium(IV) isopropoxide with acetic acid. *J Therm Anal Calorim.* 2004;75:13–24.
20. Camprostrini R, Ischia M, Palmisano L. Pyrolysis study of sol–gel derived TiO<sub>2</sub> powders Part I. TiO<sub>2</sub>-anatase prepared by reacting titanium(IV) isopropoxide without chelating agents. *J Therm Anal Calorim.* 2004;75:25–34.
21. Oja-Açik I, Madarász J, Krunks M, Tõnsuaadu K, Janke D, Pokol G, et al. Thermoanalytical studies of titanium(IV) acetylacetonate xerogels with emphasis on evolved gas analysis. *J Therm Anal Calorim.* 2007;88:557–63.
22. Krunks M, Madarász J, Hiltunen L, Mannonen R, Mellikov E, Niinistö L. Structure and thermal behaviour of dichlorobis(thiourea)cadmium(II), a single-source precursor for CdS thin films. *Acta Chem Scand.* 1997;51:294–301.
23. Madarász J, Bombicz P, Okuya M, Kaneko S, Pokol G. Online coupled TG-FTIR and TG/DTA-MS analyses of the evolved gases from dichloro(thiourea) tin(II). *Solid State Ionics.* 2004;172:577–81.
24. Madarász J, Bombicz P, Okuya M, Kaneko S, Pokol G. Comparative online coupled TG-FTIR and TG/DTA-MS analyses of the evolved gases from thiourea complexes of SnCl<sub>2</sub>. Tetra-chloropenta(thiourea) ditin(II), a compound rich in thiourea. *J Anal Appl Pyrol.* 2004;72:209–14.
25. Madarász J, Krunks M, Niinistö L, Pokol G. Evolved gas analysis of dichlorobis(thiourea)zinc(II) by coupled TG-FTIR and TG/DTA-MS techniques. *J Therm Anal Calorim.* 2004;78:679–86.
26. Madarász J, Pokol G. Comparative evolved gas analyses on thermal degradation of thiourea by coupled TG-FTIR and TG/DTA-MS instruments. *J Therm Anal Calorim.* 2007;88:329–36 (and references therein).
27. Venz PA, Frost RL, Bartlett JR, Woolfrey JL, Kloprogge JT. Thermal transformations of titania hydrolysates prepared from tetraisopropoxytitanium(IV). *Thermochim Acta.* 2000;346:73–82.
28. Hardy A, D’Haen J, Van Bael MK, Mullens J. An aqueous solution-gel citratoperoxo-Ti(IV) precursor: synthesis, gelation, thermo-oxidative decomposition and oxid crystallization. *J Sol–Gel Sci Technol.* 2007;44:65–74.
29. Madarász J, Okuya M, Kaneko S, Pokol G. Thermal behavior of Ti-precursor sols for porous TiO<sub>2</sub> thin films. *Solid State Ionics.* 2004;172:515–8.
30. Madarász J, Okuya M, Varga PP, Kaneko S, Pokol G. TG/DTA-MS studies on titania precursors with low content of organics for porous thin films of TiO<sub>2</sub>. *J Anal Appl Pyrol.* 2007;79:479–83.
31. Madarász J, Kaneko S, Okuya M, Pokol G. Comparative evolved gas analyses of crystalline and amorphous titanium(IV)oxo-hydroxo-acetylacetonates by TG-FTIR and TG/DTA-MS. *Thermochim Acta.* 2009;489:37–44. doi: [10.1016/j.tca.2009.01.020](https://doi.org/10.1016/j.tca.2009.01.020).
32. Crişan M, Brăileanu A, Răileanu M, Zaharescu M, Crişan D, Drăgan N, et al. Sol–gel S-doped TiO<sub>2</sub> materials for environmental protection. *J Non-Cryst Solids.* 2008;354:705–11.
33. Madarász J, Brăileanu A, Pokol G. Comprehensive evolved gas analysis of amorphous precursors for S-doped titania by in situ TG-FTIR and TG/DTA-MS. Part 1. Precursor from thiourea and titanium(IV)-isopropoxide. *J Anal Appl Pyrol.* 2008;82:292–7.
34. Madarász J, Brăileanu A, Crişan M, Pokol G. Comprehensive evolved gas analysis of amorphous precursors for S-doped titania by in situ TG-FTIR and TG/DTA-MS: Part 2. Precursor from thiourea and titanium(IV)-n-butoxide. *J Anal Appl Pyrol.* 2009;85:549–56. doi: [10.1016/j.jaap.2008.10.017](https://doi.org/10.1016/j.jaap.2008.10.017).
35. NIST Chemistry Webbook Standard Reference Database No 69, June 2009 Release. <http://webbook.nist.gov/chemistry>.
36. Spectral Database for Organic Compounds, SDBS, National Institute of Advanced Industrial Science and Technology, Japan. [http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct\\_frame\\_top.cgi](http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi).
37. Ischia M, Camprostrini R, Lutterotti L, Gracia-Lopez E, Palmisano L, Schiavello M, et al. Synthesis, characterization and photocatalytic activity of TiO<sub>2</sub> powders prepared under different gelling and pressure conditions. *J Sol–Gel Sci Technol.* 2005;33:201–13.
38. Ren L, Huang X, Sun F, He X. Preparation and characterization of doped TiO<sub>2</sub> nanodandelion. *Mater Lett.* 2007;61:427–31.
39. Nishide T, Tanaka T, Yabe T. Temperature programmed desorption analysis of sol-gel-derived titania films. Design of a sol preparation procedure. *J Therm Anal Calorim.* 2007;90:373–8.
40. Toshikazu N, Takayuki Y, Nobuyoshi M, Makiko S. Analysis of firing processes of titania gel films fabricated by sol–gel processes. *Thin Solid Films.* 2004;467:43–9.
41. International Centre for Diffraction Data (ICDD), Powder Diffraction File (PDF), PDF-2 Release 2008.