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PYROLYSIS STUDY OF SOL–GEL DERIVED TiO_2 POWDERS

Part II. TiO_2-anatase prepared by reacting titanium(IV) isopropoxide with oxalic acid

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Abstract

Homogeneous TiO_2 powders were obtained, via sol–gel method, hydrolysing titanium(IV) isopropoxide, previously reacted with oxalic acid in order to better control the gelling process. The characterization of the amorphous TiO_2 powders was carried out by using different techniques such as FT-IR, XRD and N_2 adsorption analysis. Coupled thermogravimetric (TG) gas chromatographic (GC) and mass spectrometric (MS) analyses were performed to quantify the organic content present in the titania gel and its release during pyrolysis. A detailed semiquantitative analysis of the evolved chemical species from TG-MS data allowed to describe the chemical composition of the TiO_2 gel and the chemical rearrangements occurring in matrix during pyrolysis up to its crystallization to anatase form at 530°C.

Keywords: pyrolysis study, thermogravimetric-mass spectrometric coupled analyses, TiO_2 gel

Introduction

As preliminary introduced in the first part [1], the sol–gel method allows the preparation of TiO_2 powders of tailored morphological features by controlling suitable operative parameters [2, 3]. In particular, the control of the hydrolysis and condensation rate reactions may be realized modifying the titanium alkoxide precursor by reaction with appropriate chelating ligands [4, 5]. The use of these last species leads to an increase of the titanium co-ordination number transforming initial monomeric tetracoordinate units into less reactive oligomeric species. In this case, the hydrolysis of titanium oligomeric species can be easily carried out by using a stoichiometric H_2O/Ti molar ratio and working under a strong acid medium. Indeed, these operative conditions favor a preferential linear growth of the Ti–O–Ti polymeric chains, which promotes the formation of TiO_2 gel with high surface area.

In the first contribution we have shown a new process of our experimental data collected in TG-MS and TG-GC-MS measurements. This data elaboration leads to

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determine, with an acceptable approximation, the chemical composition of the TiO_2 gel obtained reacting the titanium alkoxide precursor with formic acid. In that case, the amorphous TiO_2 gel mainly consisted of titanium atoms bonded with two bridging oxygen atoms and bearing both a hydroxyl group and a formate ligand. In particular, the presence of this ligand, with its capability to be bridging coordinated between two Ti atoms, fruitfully contributes to cross-linking the Ti–O–Ti chains, which is required for the formation of the gel network.

In this second paper the experimental results and data processed by this semi-quantitative TG-MS evaluation model are presented for a TiO_2 sample obtained modifying the isopropoxide titanium precursor by reaction with a stronger chelating agent such as the oxalic acid.

Experimental

Chemicals

Titanium isopropoxide (98.5%) was purchased from ABCR, oxalic acid (99%) and 2-propanol (99%) were Aldrich reagent grade products. The 1 M HCl solution was obtained by dilution of a Carlo-Erba pure reagent grade 37% (d=1.186 g cm^{-3}) HCl solution. All chemicals were used as received without any further purification.

Instrumentation

Instruments and operative condition employed in the sample characterization by using: N_2 adsorption measurements, recording of infrared- and X-ray diffraction spectra, determination of thermogravimetric (TG) and differential thermal analyses (DTA) coupled with gas-chromatographic (GC) and mass spectrometric (MS) measurements, are all described in part 1 [1].

Results and discussion

Synthesis of sample

6.53 mL of $Ti(OCH(CH_3)_2)_4$ ($2.19\cdot10^{-2}$ mol) were initially diluted with 16.8 mL of 2-PrOH (0.219 mol), working under nitrogen flow. 1.971 g of HO_2CCO_2H ($2.19\cdot10^{-2}$ mol) were then added to the alkoxide precursor under vigorous stirring. After complete solubilization, 0.40 mL of a 1M HCl solution (corresponding to $2.19\cdot10^{-2}$ mol of H_2O and $4\cdot10^{-4}$ mol of H_3O^+), diluted with 16.8 mL of 2-propanol (0.219 mol), were added dropwise, obtaining a fine emulsion. The white emulsion, kept under stirring for 2 h and then processed in air, changed to a transparent solution affording a homogeneous gel within 4 days. Operative sol–gel parameters consisted in the following molar ratios Ti-alkoxide (precursor):oxalic acid (ligand):2-propanol (solvent):water:hydrochloric acid (hydrolysis catalyst)=1:1:20:1:0.0184. The gel was milled to fine powders, dried at room temperature for 3 days, and then under vacuum (10^{-2} mBar) for 2 days. Dried gel sample was labelled: TiO_2–Ox.

Specific surface area and porosity determinations, FTIR and XRD data

Nitrogen adsorption measurement, for TiO_2–Ox sample, gave rise to an isotherm curve typical of a macroporous material. Data, processed by B.E.T. and B.J.H. equations, indicate specific surface area and average pore diameter values of 18 $m^2 g^{-1}$ and 24.4 nm, respectively [6, 7].

FT-IR spectrum of dried TiO_2–Ox powders shows the usual intense broad bands due to the –O–H stretching and Ti–O–Ti network absorption at ca. 3300 and 600 cm^{-1}, respectively [8]. Other two intense bands are detected at 1714 and 1678 cm^{-1}, with less intense peak at 813 cm^{-1}, attributed to the Ti-coordinated oxalate groups. Weak broad signals, arising from not-hydrolysed isopropoxide groups, are observed at ca. 2990, 1395, 1270 and 1105 cm^{-1} [9, 10]. The signals, correlated to the organic TiO_2 gel moiety, totally disappear in samples heated at temperatures higher than 550°C.

XRD data, carried out on the starting gel, indicate the presence of an amorphous material, whereas the diffraction peaks pattern of the anatase form is detected for powders heated at temperatures higher than 500°C, according to JCPDS card n° 21–1272.

Pyrolysis study

Thermogravimetric analysis of TiO_2–Ox gel was characterised by two consecutive mass losses, as shown in Fig. 1. The first loss (80–360°C range, intensity 45.9%) is divided in two events centred at 125 and 245°C; the latter is preceded by a shoulder at 185°C, as shown in DTG curve. The second mass loss (360–950°C range, intensity 5.0%) shows two subsequent modest events at 435 and 540°C. DTA curve shows a more intense endothermic band at 125°C, followed by a shoulder at 225°C and an exothermic peak at 535°C.

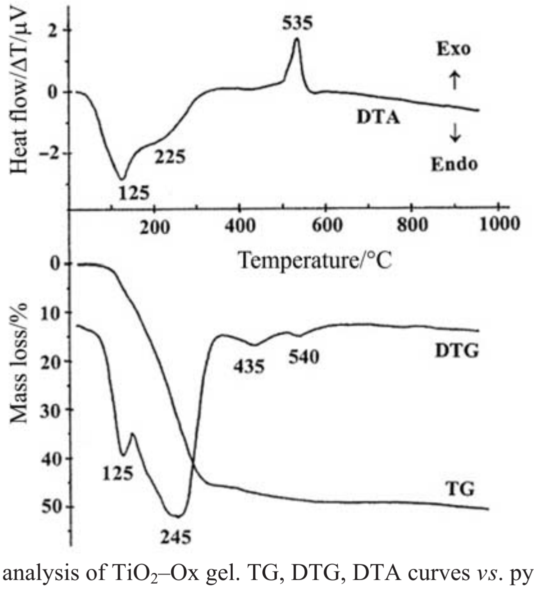


Fig. 1 Thermal analysis of TiO_2–Ox gel. TG, DTG, DTA curves *vs.* pyrolysis temperature

In Fig. 2 the TIC curve, which trend well reproduces the reflected image of DTG curve, shows in the 80–370°C range two intense overlapped peaks, centred respectively at 125 and 245°C, followed by two very small bands at 435 and 540°C. Mass spectra, recorded in TG-MS analysis (Fig. 2), show the main evolution of H_2O (*m*/*z* 18, 17 signals) with lower amounts of $CH_3CH{=}CH_2$ (*m*/*z* 42, 41, 39 signals) for the first peak at 125°C, whereas for the second one centred at 245°C, the release of CO_2 (*m*/*z* 44 signal), CO (*m*/*z* 28 signal) with very low amounts of H_2O. At higher temperatures, the release of H_2O is detected at 435°C, CO_2 and CO at 540°C.

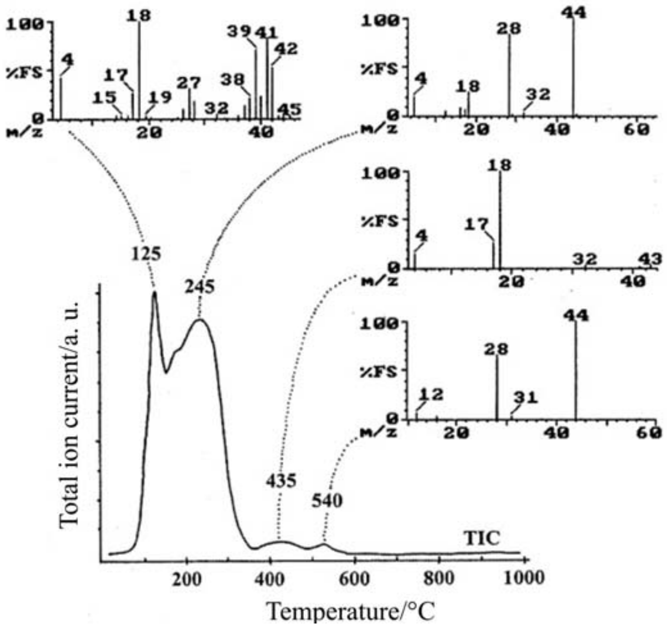


Fig. 2 Total ion current of evolved gas phase of TiO_2–Ox gel in TG-MS coupled analyses. In the insets mass spectra recorded inside the TIC peaks

Gas chromatographic elutions of gas sampling carried out at the above temperatures (TG-GC-MS measurements) confirm the evolution of these species, as shown in Fig. 3 and summarized in Table 1. At 125°C water is formed by condensation of ≡Ti–OH groups [11], propene by the β-elimination of $\equiv Ti–O–CH(CH_3)_2$ groups yielding new ≡Ti–OH units, whereas the minor amount of 2-propanol by reaction between isopropyl and hydroxyl groups:

$$\equiv\text{Ti–OH+HO–Ti}\equiv \rightarrow \equiv\text{Ti–O–Ti}\equiv\text{+H}_2\text{O}(g) \qquad (1)$$

$$\equiv\text{Ti–OCH(CH}_3)_2 \rightarrow \equiv\text{Ti–OH+CH}_3\text{–CH=CH}_2(g) \qquad (2)$$

$$\equiv\text{Ti–OH+(CH}_3)_2\,\text{CH–O–Ti}\equiv \rightarrow \equiv\text{Ti–O–Ti}\equiv\text{+(CH}_3)_2\text{CHOH}(g) \qquad (3)$$

Table 1 Chemical species detected in gas chromatographic elutions (TG-GC-MS analyses) during pyrolysis of TiO_2–Ox sample; 100 μL gas phase sampling

Temperature sampling/°C	Relative mass loss intensity in the TG curve/%	Capillary column	Identified chemical species[a,b] (intensity)[c]
125	8.2	PoraPlot Q	H_2O (h), $CH_3CH=CH_2$ (m), 2-PrOH (l)
		OV1	$CH_3CH=CH_2$ (m), H_2O (h), 2-PrOH (l)
245	37.7	PoraPlot Q	CO (h), CO_2 (h), H_2O (l), $CH_3CH=CH_2$ (t)
		OV1	[$CO+CO_2$] (h), H_2O (l)

[a] Chemical species are reported in order of elution

[b] Chemical species eluted inside the same chromatographic peak are reported in square brackets

[c] The intensity of the eluted species, inside the same gas chromatogram, are approximately evaluated as: h=high; m=medium; l=low, t=traces

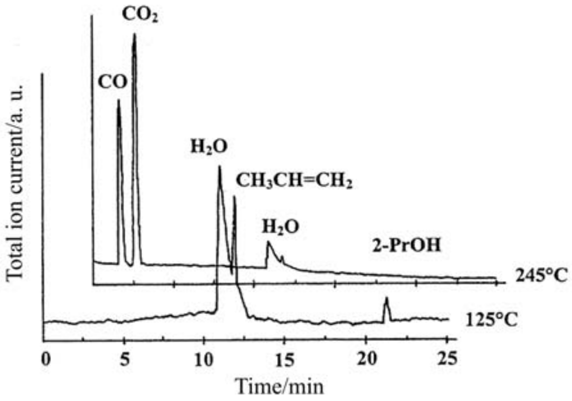
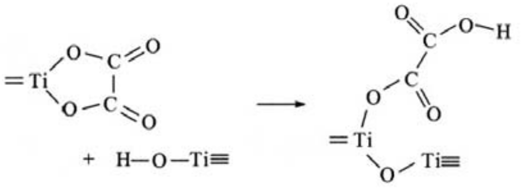


Fig. 3 TG-GC-MS analyses: gas chromatographic elutions of the gas phase evolved and sampled at 125 and 245°C, respectively, in the pyrolysis of TiO_2–Ox gel

In the TG-GC-MS analysis at 245°C, the evolution of CO, CO_2 and the minor amount of H_2O could arise from the decomposition of the oxalate groups, which could be mainly bi-coordinated or even mono-coordinated to titanium atoms, by reaction with ≡Ti–OH groups, as proposed in the following reactions:



(4)

$$\equiv\text{Ti–O–OCCO–OH} \rightarrow \equiv\text{Ti–O–H}+\text{CO}(g)+\text{CO}_2(g) \tag{5}$$

$$\equiv\text{Ti–O–OCCO–OH}+\text{HO–Ti}\equiv \rightarrow \equiv\text{Ti–O–Ti}\equiv+\text{CO}(g)+\text{CO}_2(g)+\text{H}_2\text{O}(g) \tag{6}$$

At the highest temperatures, water, which characterizes the loss at 435°C, could derive from the condensation of the previously formed ≡Ti–OH groups, whereas at 540°C the evolution of CO_2 and CO could be justified by the decomposition of residual oxalate aniones which could result more strongly bridging-coordinated to titanium atoms:

$$\equiv\text{TiO–OCCO–O–Ti}\equiv \rightarrow \equiv\text{Ti–O–Ti}\equiv+\text{CO}(g)+\text{CO}_2(g). \tag{7}$$

The release of these chemical species during pyrolysis can be followed by the curves obtained by plotting the signals of appropriate ions, as presented in Fig. 4. H_2O evolution (*m*/*z* 18) is described by a first more intense band centred at 127°C, a shoulder at 210°C and a less intense band at 435°C. This last contribution gives rise of the third mass loss of the sample. The small release of 2-propanol (*m*/*z* 59) gives a narrow band centred at 103°C. The evolution of propene (*m*/*z* 42 or 41) presents a sharp peak at 125°C, which also generates the form of the first TIC peak. CO (*m*/*z* 28) and

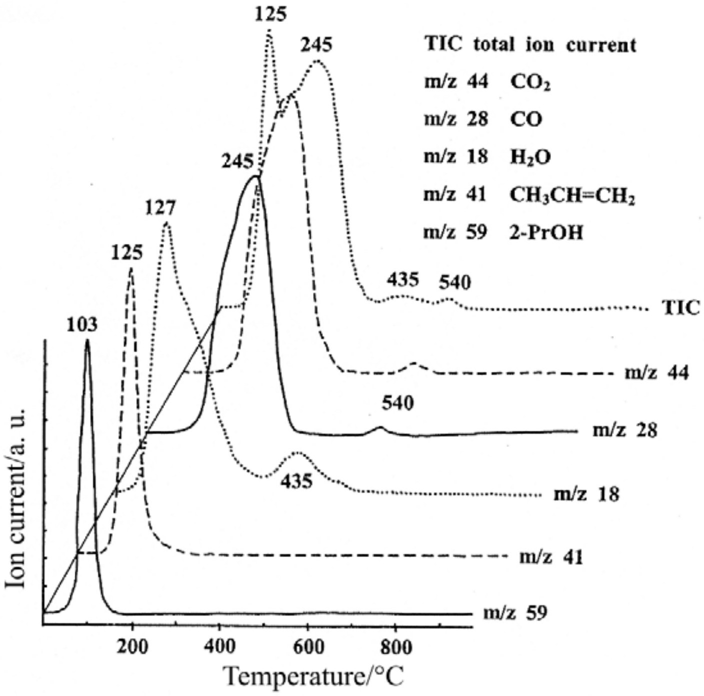


Fig. 4 Ion currents of selected ions used to monitor the evolution of evolved species during TiO_2–Ox gel pyrolysis

CO_2 (*m*/*z* 44) are contemporaneously released with a first intense event, centred at 245°C (shoulder at 200°C), followed with a second one at 540°C, forming respectively the trend of the second and last TIC bands. These data deserve some comments. The perfect overlapping of *m*/*z* 28 and 44 ion current trends indicates that both CO and CO_2 evolutions arise from the same event, which can be associated to the decomposition of an oxalate group, independently of its kind of coordination to the titanium atoms. 2-Propanol is the first species released in the gas phase, but its development, requiring the availability of ≡Ti–OH groups, is quickly interrupted by increasing the temperature as it can be observed also for water. These results indicate that the hydroxyl groups, initially prone to the Eqs (1) and (3), can be subsequently involved in other kinds of reactions. At temperatures ca. 100°C lower with respect to the other studied gels, the early development of propene, due to thermal elimination of isopropoxide groups, is probably due to a catalytic contribution. To this regard, the relevant presence of oxalate moieties inside the TiO_2 matrix could activate a hydrogen transfer from the isopropoxide group and the subsequent release of the unsaturated hydrocarbon by an intermolecular interaction. By comparing the trends of *m*/*z* 18 with *m*/*z* 28 and 44 signals, some interesting symmetries of the relative ion currents can be noted. In particular, a complementary increase of CO and CO_2 evolution, referred to the decrease of water, is revealed. These findings suggest that ≡Ti–OH groups are now engaged by oxalate groups (Eq. (4)). This ligand is probably mainly coordinated in chelating manner to a single Ti atom, because a dilute solution of the alkoxide titanium precursor was used to react with the oxalate acid. Subsequently, the more unstable mono-coordinate oxalate group could decompose, as described by Eqs (5) and/or (6), evolving CO and CO_2 in stoichiometric ratio. Moreover, in the direct thermal decomposition of oxalate ligand (Eq. (5)), the formation of new ≡Ti–OH groups can justify the following water evolution observed at temperatures close to 435°C. Finally, the development of CO and CO_2 during the last event in the TIC curve can be attributed to the decomposition of the residual oxalate groups, probably bridging bonded between different Ti–O–Ti chains, during the structural TiO_2 rearrangements leading to anatase crystallization.

The perfect overlapping of the total ion current trend with the curve obtained by adding the representative ions of all the relevant detected species confirms that a whole description of the pyrolysis process has been successfully achieved.

A semiquantitative evaluation of pyrolysis data

As described in part 1 [1], a semiquantitative evaluation of the pyrolysis process was calculated from TG-MS analysis, which was carried out on 17.7 mg of dried TiO_2–Ox gel yielding 8.7 mg of residual solid and 9.0 mg of evolved gas species. The main chemical compounds present in the gas mixture were: H_2O, CO, CO_2, propene and 2-propanol. Table 2 summarizes: a) all the fragmentation ions (i) detected in the mass spectrum of these substances (j) and their relative intensity, $r(i)_j$, as recorded in the TG-GC-MS measurements; b) the integrated values of the m/z ion current for the ions used both to monitor the single chemical species in the TG-MS analysis ($Im/z(i)_{\text{TG–MSdata}}$) and the ones used in data processing ($Im/z(i)_j$); c) the values which estimate the total amount of each released species, $A(j)$, obtained considering the above parameters.

First, the amounts of released 2-propanol and water were directly calculated from the integrated values of their representative ions $Im/z(59)_{\text{TG-MSdata}}=0.14\cdot10^6$ and $Im/z(18)_{\text{TG-MSdata}}=146.62\cdot10^6$, respectively. Then, the evolved propene was estimated from the integrated signal of $m/z(41)$ subtracting the contribution arising from 2-propanol:

$$Im/z(41)_{\text{propene}} = Im/z(41)_{\text{TG-MSdata}} - Im/z(41)_{\text{2-propanol}} = \\ 40.69\cdot10^6 - 0.35\cdot10^6 = 40.34\cdot10^6.$$

Analogously, CO_2 amount was calculated considering:

$$Im/z(44)_{\text{carbon dioxide}} = Im/z(44)_{\text{TG-MSdata}} - Im/z(44)_{\text{2-propanol}} = \\ 270.26\cdot10^6 - 0.14\cdot10^6 = 270.12\cdot10^6.$$

Finally, released CO was obtained from the integrated signal of m/z 28 ion considering the contribution of 2-propanol, propene and CO_2:

$$Im/z(28)_{\text{carbon monoxide}} = \\ Im/z(28)_{\text{TG-MSdata}} - Im/z(28)_{\text{propene}} - Im/z(28)_{\text{2-propanol}} - Im/z(28)_{\text{carbon dioxide}} = \\ 196.07\cdot10^6 - 1.83\cdot10^6 - 0.28\cdot10^6 - 18.42\cdot10^6 = 175.54\cdot10^6.$$

Table 2 Data from mass spectra of pure chemical species and from integrated values of m/z ion currents

Chemical species, representative ion [integrated m/z value obtained by TG-MS analysis, a.u.]	M/Z ions from mass spectra of pure substances in TG-GC-MS analyses; (peak height/mm) [integrated m/z signal value, a.u.][a]	(Sum of the peak heights/mm) [integrated amount value of the chemical species, a.u.]
H_2O, 18 [$146.62\cdot10^6$]	16 (2); 17 (21); 18 (88) [$146.62\cdot10^6$]	(111) [$184.94\cdot10^6$]
2-Propanol, 59 [$0.14\cdot10^6$]	14 (2); 15 (7); 19 (6); 27 (20); 28 (8) [$0.28\cdot10^6$]; 29 (13); 31 (11); 32 (2); 39 (10); 40 (2); 41 (10) [$0.35\cdot10^6$]; 42 (4); 43 (18); 44 (4) [$0.14\cdot10^6$]; 45 (88) [$3.07\cdot10^6$]; 59 (4) [$0.14\cdot10^6$]	(209) [$7.28\cdot10^6$]
Propene, 41 [$40.69\cdot10^6$]	15 (1); 19 (2); 20 (1); 26 (11); 27 (38); 28 (4) [$1.83\cdot10^6$]; 32 (3); 36 (2); 37 (11); 38 (16); 39 (60); 40 (28); 41 (88) [$40.341\cdot10^6$]; 42 (58); 43 (4)	(327) [$149.91\cdot10^6$]
CO_2, 44 [$270.26\cdot10^6$]	12 (2); 16 (3); 28 (6); [$18.42\cdot10^6$]; 44 (88) [$270.12\cdot10^6$]; 45 (1)	(100) [$309.96\cdot10^6$]
CO, 28 [$196.07\cdot10^6$]	12 (2); 28 (88) [$175.54\cdot10^6$]; 29 (2)	(92) [$183.52\cdot10^6$]

[a] For the sake of conciseness, only the values used in the processing data are summarized

Table 3 shows the chemical composition of the gas phase evolved during pyrolysis and the absolute amounts of each released species calculated from the sample mass loss. The 'degree of identification' (given in %) of the released gas mixture, obtained dividing the sum of the absolute amounts of each compound by the integrated value of the TIC signal (I_{TIC}=851.63·10^6), results 98% indicating the reliability of this procedure.

Table 3 Chemical composition of gas mixture (9.0 mg) evolved in the whole TiO_2–Ox pyrolysis process

Chemical species (molecular mass)	Molar/%	Mass/%	Moles
2-Propanol (60)	0.9	1.6	$2.30\cdot10^{-3}$
H_2O (18)	22.2	11.6	$5.80\cdot10^{-2}$
Propene (42)	18.0	21.9	$4.70\cdot10^{-2}$
CO (28)	22.0	17.9	$5.76\cdot10^{-2}$
CO_2 (44)	36.9	47.0	$9.63\cdot10^{-2}$

In the hypothesis that the 8.7 mg residual solid (pyrolyzed up to 1000°C) corresponds to 0.1088 mmol of pure TiO_2, the same amount of titanium atoms have to be present in the initial gel. Moreover, considering that the release of: a) one water molecule required the reaction between two hydroxyl groups (Eq. (1)), b) one 2-propanol molecule required the condensation between a hydroxyl and an isopropoxide group (Eq. (3)), c) one propene molecule required the consumption of one isopropoxide group (Eq. (2)), d) the pyrolysis of an oxalate groups produced in any case one molecule of carbon monoxide and one of carbon dioxide (Eqs (4)–(7)), a presence of 0.1184, 0.0769, and 0.0493 mmol of $\equiv$Ti–OH, =Ti–$(OCO)_2$ and $\equiv$Ti–$OCH(CH_3)_2$ terminal groups, respectively, were calculated in the initial TiO_2 gel. Consequently, if all the oxalate groups are considered bi-coordinated to the titanium atoms, 0.0569 mmol of bridging oxygen atoms were calculated from the 0.4352 mmol of titanium bonds and the 0.3215 mmol of bonds with terminal groups.

In this case, the initial gel composition,

$$TiO_{0.52}(OH)_{1.09}(OCH(CH_3)_2)_{0.45}(O_2C_2O_2)_{0.71},$$

affords a mass balance of 17.8 mg in comparison with the experimental 17.7 mg (relative error <1%).

On the other hand, if the oxalate groups are all considered mono-coordinated, 0.0953 mmol of bridging oxygen atoms were calculated, leading to 18.5 mg of initial gel (relative error 4.5%) with nominal composition

$$TiO_{0.88}(OH)_{1.09}(OCH(CH_3)_2)_{0.45}(OCOCOOH)_{0.71}.$$

Conclusions

The sol–gel synthesis allowed the easy preparation of TiO_2 gel powders particularly when the titanium isopropoxide precursor was modified by a coordination ligand as the oxalate group. The amorphous TiO_2 powders, still containing a relevant amount of the organic moiety, was converted to polycrystalline TiO_2-anatase powders by heat treatment at temperatures higher than 500°C. The detailed pyrolysis study, carried out by coupling the thermal analysis with gas chromatographic and mass spectrometric measurements of the released gas phase, allowed to depict the chemical rearrangements occurring in the TiO_2 network during heating. In this sample the typical condensation between residual ≡Ti–OH and isopropoxide groups was early interrupted by the beginning of the elimination reaction with release of propene, followed by the hydrolysis of the main fraction of the coordinated oxalate groups and their decomposition to CO and CO_2 at temperatures close to 250°C. Indeed, this experimental data did not allow to discriminate the relative amounts of oxalate groups differently coordinated to titanium atoms in the starting gel, but both in the mono- and bi-dentate case an acceptable mass balance describing the initial gel composition was obtained. Finally, the complete matrix 'inorganication' of this TiO_2–Ox sample occurred only at higher temperatures: anatase phase crystallization was observed at 535°C, although the most abundant release of organic fraction was detected in the early stages of the pyrolysis, i.e. in the 100–300°C range.

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