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PYROLYSIS STUDY OF SOL–GEL DERIVED TiO_2 POWDERS
Part I. TiO_2-anatase prepared by reacting titanium(IV) isopropoxide with formic acid

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Abstract

A homogeneous TiO_2 gel sample was prepared, via sol–gel method, hydrolysing titanium(IV) isopropoxide, previously modified by reaction with formic acid. The amorphous TiO_2 gel was characterized using various techniques such as FT-IR, XRD and N_2 adsorption analysis. Thermoanalyses (TG, DTA) coupled with gas chromatographic (GC) and mass spec trometric measurements (MS), by means of a home-assembled instrumental interfaces, were performed in order to quantify the organic component still present in the titania gel and its release during pyrolysis. Several chemical species were evolved and detected in gas phase for temperatures up to 350°C, before crystallization of TiO_2-anatase.

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

Introduction

Polycrystalline TiO_2-anatase powders are materials of relevant interest in photocatalytic processes and in particular to photodegrade organic species in liquid–solid systems [1–4]. The photocatalytic efficiency depends on the preparation method of the catalyst [5] and its thermal treatment, which significantly influence structural and surface properties [6–9]. The sol–gel method is a versatile approach to prepare TiO_2 anatase with tailored morphological features by adjustment of the operative conditions, which control the hydrolysis and condensation reactions of suitable titanium alkoxide precursors [10]. An improvement in the preparation of high surface area TiO_2 gels is reached by previously reacting the titanium precursors with chelating species, which can modify the coordination sphere of titanium atoms decreasing their intrinsic bent *vs*. hydrolysis [11, 12].

To this aim, we prepared some TiO_2 gels studying the effects of various chelating ligands on titanium(IV) isopropoxide gelled under strong acidic medium. Indeed, the use of such modified Ti-precursors leads to an increase of the organic fraction remaining in the TiO_2 matrices which reduces the catalytic performance of these mate-

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rials [13]. For this reason, a particular attention is devoted to the pyrolysis study of these TiO_2 gels in order to compare the chemical nature of the organic moiety and its release from the amorphous TiO_2 matrices during heat treatment [14, 15]. This treatment leads to the crystallization to the TiO_2-anatase form, which generally is the most photoactive phase [16]. The results of this work are divided in some different contributions, in which the study of each kind of TiO_2 sample will be described and a particular aspect of the research will be reported.

In this first paper we would like to present a new processing of the pyrolysis data, that usually have been in previous studies simply recorded by means of coupled thermogravimetric, gas chromatographic and mass spectrometric measurements [17–19]. This data processing allows the description of the chemical composition of the initial TiO_2 gel matrix from the semi-quantitative analysis of the evolved gas phase in the case of the sample obtained reacting titanium isopropoxide with formic acid.

Experimental

Chemicals

Titanium isopropoxide (98.5%) was purchased from ABCR, formic acid (96%) 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

Specific surface area determinations and pore size distributions were measured on an ASAP 2010 Micromeritics apparatus. N_2 adsorption was performed at –196°C, evaluating the equilibrium points inside 0.05–0.33 $p/p°$ range by B.E.T. and B.J.H. equations [20, 21].

FTIR spectra were recorded on a Nicolet 5 DXC Fourier-transform infrared spectrometer in the 4000–400 cm^{-1} range; powdered samples were analyzed in KBr pellets, working in transmission mode and averaging 64 scans.

XRD analyses were carried out at room temperature in θ-2θ reflection mode using a Rigaku geigerflex diffractometer with CuK_α radiation and a diffracted-beam graphite focusing monochromator. Samples were analysed packing the powders in a glass holder and the intensity data were measured by step scanning in the 2θ range between 10 and 80°, with 2θ step size of 0.05° and acquisition time of 2 s per point.

Thermogravimetric (TG) and differential thermal analyses (DTA) were performed on a LabSys Setaram thermobalance operating in the range 20–1000°C, with a heating rate of 10°C min^{-1}, under 100 mL min^{-1} He flow. Typically, 20–40 mg of powdered samples were analysed using a 100 μL alumina crucible and α-Al_2O_3 as reference.

Gas chromatographic analyses were carried out on a HRGC Carlo Erba Instruments chromatograph, using a quadrupole mass spectrometer as detector. Chromatographic elutions were performed on various capillary columns using He as carrier gas (20 kPa inlet pressure), with a temperature program: 30°C for 5 min, followed by 5°C min^{-1} heating rate up to 200°C, held for 15 min. OV1 (Mega) column (25 m, 0.32 mm) was used to separate volatile oxygenate species, whereas, PoraPlot Q (Chrompack) column (25 m, 0.32 mm) was employed to better separate light hydrocarbons. Gas phase sampling was carried out by means of a GR8 Bimatic thermostatted microvalve (T=130°C) with a volume injection of 100 μL.

Electron impact mass spectra (70 eV) were recorded using a VG-QMD-1000 Carlo Erba Instruments quadrupole mass spectrometer. Spectra, scan from 3 to 400 amu, were continuously registered and stored with frequency 1 scan s^{-1}.

Thermogravimetric mass spectrometric gas chromatographic coupled measurements

The pyrolysis study was performed with two types of instrumental interfaces, realized by modifying the gas inlet system of the thermobalance [22, 23]. Gas species, released from the solid sample during TG-MS analysis, were drawn into an alumina tube fixed inside the furnace of the thermobalance close to the sample crucible and then connected to a capillary silica column heated at 300°C. The gases were then directly sucked into the ionization chamber of the mass spectrometer. This TG-MS interface gives: (i) the graph of the total ion current (TIC), obtained from the contribution of all ions present in each recorded mass spectra, plotted *vs*. time (or pyrolysis temperature), whose trend allows to detect any chemical species released from the sample; (ii) the plot of a selected m/z ion current (IC), which could monitor the evolution of a single specific molecular species (during the whole pyrolysis), if this ion arises from the fragmentation pattern of that chemical species only; (iii) the integrations of the m/z ion currents *vs*. time, calculated by the mass spectrometer software (in automatic or manual mode), yielding integrate values related to a quantitative information of those detected ion species.

A second instrumental interface, labelled TG-GC-MS, was realized by connecting the capillary silica column to the inlet port of the microsample valve. In this case, an external vacuum pump continuously sucked a fraction of the gas flow from the thermobalance through the valve, whereas, an appropriate gas chromatographic capillary column was connected to the outport of the valve. Gas sample injections were made for temperatures corresponding to the most important mass losses during TG analyses. This second instrumental configuration allows: (i) to separate different compounds released during the same mass loss; (ii) to identify released chemical species on the basis of their different retention times and mass spectra.

Results and discussion

Synthesis of sample

3.73 mL of $Ti(OCH(CH_3)_2)_4$ [$1.25\cdot10^{-2}$ mol] were first diluted with 9.6 mL of 2-PrOH (0.125 mol), working under nitrogen flow. To this solution 0.47 mL of HCOOH ($1.25\cdot10^{-2}$ mol) were carefully added under vigorous stirring. After 10 min, 0.23 mL of a 1M HCl solution (corresponding to $1.25\cdot10^{-2}$ mol of H_2O and $2.3\cdot10^{-4}$ mol of

H_3O^+), diluted with 9.6 mL of 2-propanol (0.125 mol), were added dropwise to the modified titanium alkoxide solution yielding a fine white emulsion. The emulsion, kept under vigorous stirring for 2 h and then processed in air, turned to a clear solution affording a homogeneous gel within 4 days. Operative sol–gel parameters consisted in the following molar ratios Ti-alkoxide (precursor):formic acid (ligand): 2-propanol (solvent):water:hydrochloric acid (hydrolysis catalyst)=1:1:20:1:0.0184. Gel was milled to fine powders, dried at room temperature for 7 days, and then under vacuum (10^{-2} mBar) for 2 days. Dried gel sample was labelled: TiO_2–Fo.

Specific surface area and porosity determinations, FTIR and XRD data

N_2 adsorption measurement, carried out on the white powders of TiO_2–Fo gel, shows an isotherm curve typical of a mesoporous material. Data, processed by B.E.T. and B.J.H. equations, give specific surface area and average pore diameter values of 480 m^2 g^{-1} and 2.7 nm, respectively.

FT-IR spectrum of dried TiO_2–Fo specimen shows two intense broad bands, centred at ca. 3300 and ca. 600 cm^{-1}, due to the –O–H stretching and Ti–O–Ti network absorption, respectively [24]. Other strong peaks are detected at 1562 and 1340 cm^{-1}, which can be attributed to the Ti-coordinated formate ligand [25]. Absorption due to not-hydrolysed isopropoxide groups are observed at 2975, 2932, 2873, 1129 and 1011 cm^{-1} [26, 27]. The signals, correlated to the organic TiO_2 gel moiety, disappear in samples heated at temperatures higher than 340°C.

As shown by XRD spectra, dried gel is an amorphous powder, any heat treatments at temperatures higher than 400°C led to the crystallization of TiO_2 gel in polycrystalline TiO_2-anatase form (according to JCPDS card n° 21-1272).

Pyrolysis study

As shown in Fig. 1, TG curve of TiO_2–Fo gel presents two subsequent mass losses up to 365°C of a total 32.0% intensity, followed by a 1.2% loss up to 900°C. DTG curve shows two intense bands centred at 115 and 225°C. According to these events, two endothermic bands are present in the DTA curve, followed by a sharp exothermic peak centred at 415°C.

Evolved gas phase leads to a TIC curve which exactly depicts the reflected image of DTG trend (Fig. 1). Mass spectra recorded in correspondence with the first TIC peak at 115°C show the release of 2-propanol and H_2O, whereas spectra at 225°C indicate the main presence of $CH_3CH=CH_2$, with a minor amount of CO and H_2O. Gas chromatographic elutions (TG-GC-MS analyses), for the sampling at 115°C, show the release of a large amount of 2-propanol, minor presence of H_2O and a smaller amount of isopropyl formate, as reported in Fig. 2 and summarized in Table 1. Water and alcohol arise from condensation reaction of vicinal hydroxyl and isopropoxide groups present inside the TiO_2-gel network:

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

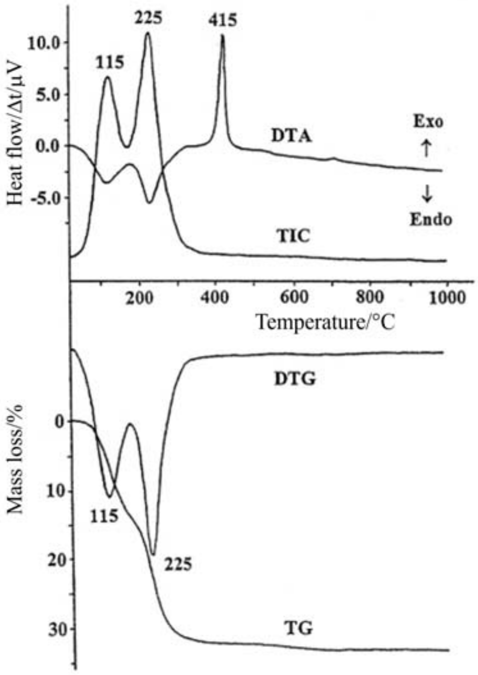

Fig. 1 Thermogravimetric mass spectrometric coupled analyses of TiO_2–Fo gel. TG, DTG, DTA curves with the total ion current (TIC) plot of the evolved gas phase *vs.* pyrolysis temperature

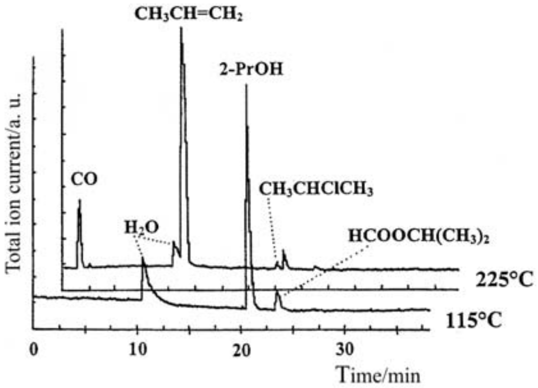

Fig. 2 Gas chromatographic elutions of the gas phase evolved at 115 and 225°C in the pyrolysis of TiO_2–Fo gel

$$\equiv Ti{-}OH + (CH_3)_2CH{-}O{-}Ti\equiv \;\rightarrow\; \equiv Ti{-}O{-}Ti\equiv + (CH_3)_2CHOH(g) \qquad (2)$$

Similarly, isopropyl formate could be formed by the condensation reaction of not hydrolyzed vicinal isopropoxide and formate groups:

$$\equiv Ti{-}OCH(CH_3)_2 + HCO{-}O{-}Ti\equiv \;\rightarrow\; \equiv Ti{-}O{-}Ti\equiv + HCO{-}OCH(CH_3)_2(g) \qquad (3)$$

Table 1 Chemical species detected in gas chromatographic elutions (TG-GC-MS analyses) during pyrolysis of TiO_2–Fo 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]
115	13.8	PoraPlot Q	H_2O (m), 2-PrOH (h), $HCOOCH(CH_3)_2$ (l)
		OV1	[H_2O+2-PrOH] (h), $HCOOCH(CH_3)_2$ (l)
225	18.2	PoraPlot Q	CO (m), H_2O (l), $CH_3CH{=}CH_2$ (h), $CH_3CHClCH_3$ (t), 2-PrOH (l), $HCOOCH(CH_3)_2$ (t)
		OV1	[CO+$CH_3CH{=}CH_2$] (h), [H_2O+2-PrOH] (l), $HCOOCH(CH_3)_2$ (t)

[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

Gas sampling at 225°C (Fig. 2) show gas-chromatograms with an intense peak for $CH_3CH{=}CH_2$ evolution, with minor amounts of CO, H_2O. As expected, at higher temperatures the final consumption of the residual isopropoxide groups happens by elimination reaction, enriching the TiO_2 matrix of new ≡Ti–OH groups:

$$\equiv Ti{-}OCH(CH_3)_2 \rightarrow \equiv Ti{-}OH + CH_3{-}CH{=}CH_2(g) \quad (4)$$

Still detected, at 225°C, is the presence of 2-propanol with traces of 2-chloropropane and isopropyl formate. The considerable release of CO in the second mass loss can be justified by the elimination of the strongly coordinated formate groups:

$$\equiv Ti{-}O{-}COH \rightarrow \equiv Ti{-}OH(s) + CO(g) \quad (5)$$

The whole pyrolysis process can be described by monitoring the evolution of all detected species through the trends of appropriate *m*/*z* signals obtained from TG-MS data analysis, as presented in Fig. 3. The release of 2-propanol, monitored by its more intense fragmentation ion $[CH_3CHOH]^+$ at *m*/*z* 45, is shown by a band centred at 110°C, with a smaller shoulder at higher temperatures just up to the second mass loss. The evolution of water, followed by its molecular ion at *m*/*z* 18, is depicted by two overlapped bands, centred at 125 and 235°, the former being more intense. Isopropyl formate, easily detected by its fragmentation ion $[HCOOCHCH_3]^+$ at *m*/*z* 73, evolves, with almost constant intensity, in a temperature range from 120 to 170°C. Propene, followed by its more intense fragmentation ion $[CH_2CHCH_2]^+$ at *m*/*z* 41 or by its molecular ion at *m*/*z* 42, is released following a sharp peak at 225°C, generating the form of the second peak in the TIC curve. Finally, CO evolution, monitored by its molecular ion at *m*/*z* 28, is described by a narrow band centred at 240°C. Moreover, a proof of the correct interpretation of the overall pyrolysis process is that the curve obtained from the sum of the single ion current of each identified chemical species exactly overlapped the experimental TIC curve; actually this occurs only when all the evolved species are considered as shown in Fig. 4.

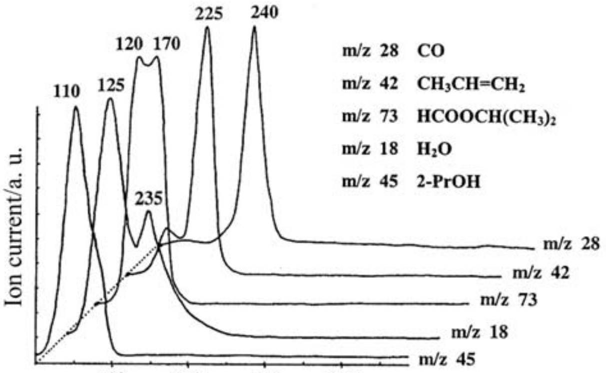

Fig. 3 Ion currents of selected ions used to represent the release of mainly evolved species during TiO_2–Fo gel pyrolysis

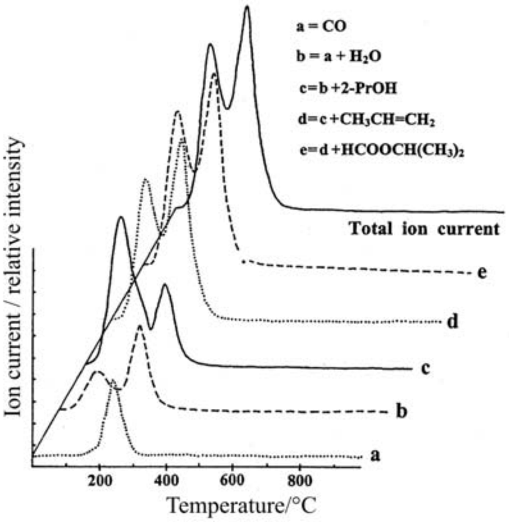

Fig. 4 Comparison between the shape of the total ion current and the ion currents obtained considering the different contribution arising from the various detected species. The intensity of each m/z ion current, representing an evolved chemical species, is multiplied for the molecular ratio value found for that species in the semiquantitative gas phase analysis during the whole pyrolysis process (Table 3)

A semiquantitative evaluation of pyrolysis data

In order to confirm the reliability of both experimental data and of the proposed chemical reactions occurring during the whole pyrolysis process, an attempt to foreseen the chemical composition and the mass balance of the initial gel has been made from a semiquantitative analysis of the evolved gas phase, elaborating the data recorded during the TiO_2–Fo TG-MS measurement.

Thermogravimetric analysis was carried out on 50.9 mg of dried gel yielding a residual solid of 34.0 and 16.9 mg of evolved gas. The released gas mainly consisted of 2-propanol, water, propene, carbon monoxide and isopropyl ester, whereas other species observed in lower quantity or in traces have been neglected in the following procedure. As previously showed, each chemical compound (subsequently indicated with a 'j') can be represented by an appropriate ion among the ones formed from its ionization and fragmentation process occurring during mass spectrometric analysis. Following in the text, any fragment ion will be indicated as '$m/z(i)$'. Unfortunately, some of these ions can arise from the fragmentation pathway of different molecules and this fact has to be taken into account. Table 2 shows the relative intensities of all ions, $m/z(i)$, detected in the mass spectrum (recorded in the same operative conditions) of each chemical species, j, when these compounds were eluted as pure substances in the available gas chromatographic TG-GC-MS measurements. From this global picture a correct choice of the suitable ions can be done. To approximately quantify the amount of a released species, the signal of its representative ion has been first integrated during the whole pyrolysis process extrapolating this m/z ion current trend from the TG-MS analysis. Integrated values will be indicated as '$Im/z(i)$'. Moreover, the relative intensity of this ion was calculated by considering all the peaks heights present in the mass spectrum of that compound: $r(i)_j=h(i)_j/\Sigma h(i)_j$. The total amount of that released species, indicated with '$A(j)$', has been then estimated by dividing the integrated m/z signal by the relative intensity of its representative ion: $A(j)=Im/z(i)/r(i)_j$, labelling it as integrated amount. In turn from this last value, the contribution of each ion present in the mass spectrum of that j-species can be obtained, as integrated ion current $[Im/z(i)_j]$ where $Im/z(i)_j=A(j)r(i)_j$. Finally, the molar ratio, or percentage, of each chemical species present in the evolved gas mixture can be calculated by means of the integrated amount of all compounds: $\%_{mol}(j)=100A(j)/\Sigma A(j)$. This procedure affords a gas phase semiquantitative analysis by considering the mass spectrometer as a gas chromatographic detector presenting the same sensibility in revealing any different chemical compounds.

In this work, the amount of isopropyl formate was first calculated considering the integrated signal of its representative m/z ion $Im/z(73)_{\text{TG-MSdata}}=6.12\cdot 10^6$, being this ion formed in the fragmentation process of this compound only. Similarly, water percentage was calculated from the integrated signal of its m/z 18 molecular ion $Im/z(18)_{\text{TG-MSdata}}=346.89\cdot 10^6$. Then, the percentage of 2-propanol was calculated considering the m/z 45 signal by previously subtracting from its integrated value the contribution arising from the isopropyl formate

$$Im/z(45)_{\text{2-propanol}} = Im/z(45)_{\text{TG-MSdata}} - Im/z(45)_{\text{isopropyl formate}} =$$
$$= 496.44\cdot 10^6 - 23.41\cdot 10^6 = 473.03\cdot 10^6.$$

The same procedure leads to calculate the amount of propene through the m/z 41 signal, subtracting the contribution arising from both 2-propanol and isopropyl formate

$$Im/z(41)_{\text{propene}} = Im/z(41)_{\text{TG-MSdata}} - Im/z(41)_{\text{2-propanol}} - Im/z(41)_{\text{isopropyl formate}} =$$
$$= 280.93\cdot 10^6 - 43.00\cdot 10^6 - 9.58\cdot 10^6 = 228.35\cdot 10^6.$$

Finally, the percentage of carbon monoxide was calculated considering its m/z 28 molecular ion and the contribution of this signal due to the isopropyl formate

$$Im/z(28)_{\text{carbon monoxide}} = Im/z(28)_{\text{TG-MSdata}} - Im/z(28)_{\text{isopropyl formate}} =$$
$$= 275.31\cdot 10^6 - 2.13\cdot 10^6 = 273.18\cdot 10^6.$$

The chemical composition of the gas phase evolved during the whole pyrolysis process of TiO_2–Fo sample is summarized in Table 3. From these percentages and from the intensity of the mass loss, the absolute amount of each released species has been determined. Moreover, the ratio between the sum of all integrated amounts of the detected species ($\Sigma A(j)=2452.61\cdot 10^6$) and the integrated value of the total ion current in the TG-MS analysis ($I_{TIC}=2658.29\cdot 10^6$) indicates both the 'degree of identification' (92%) of the gas mixture and the intrinsic error of this semiquantitative analysis.

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.]
CO, 28 [$275.31\cdot10^6$]	12 (2); 28 (88) [$273.18\cdot10^6$]	(92) [$285.60\cdot10^6$]
H_2O, 18 [$346.89\cdot10^6$]	16 (2); 17 (21); 18 (88) [$346.89\cdot10^6$]	(111) [$437.55\cdot10^6$]
2-Propanol, 45 [$496.44\cdot10^6$]	15 (4); 19 (3); 26 (1); 27 (9); 29 (7); 31 (5); 37 (1); 38 (2); 39 (6); 41 (8) [$43.00\cdot10^6$]; 42 (4); 43 (18); 45 (88) [$473.03\cdot10^6$]; 46 (2); 59 (4)	(162) [$870.81\cdot10^6$]
Propene, 41 [$280.93\cdot10^6$]	14 (2); 15 (3); 19 (2); 20 (2); 25 (1); 26 (6); 27 (24); 36 (2); 37 (10); 38 (16); 39 (63); 40 (22); 41 (88) [$228.35\cdot10^6$]; 42 (51); 43 (2)	(294) [$762.88\cdot10^6$]
Isopropyl ester, 73 [$6.12\cdot10^6$]	14 (1); 15 (6); 19 (4); 26 (4); 27 (35); 28 (8) [$2.13\cdot10^6$]; 29 (20); 30 (5); 31 (8); 32 (1); 37 (2); 38 (4); 39 (16); 40 (3); 41 (36) [$9.58\cdot10^6$]; 42 (42); 43 (36); 44 (2); 45 (88) [$23.41\cdot10^6$]; 46 (3); 47 (7); 59 (6); 73 (23) [$6.12\cdot10^6$]	(360) [$95.77\cdot10^6$]

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

Table 3 Chemical composition of gas mixture (16.9 mg) evolved in the whole TiO_2–Fo pyrolysis process calculated from the TG-MS data

Chemical species (molecular mass)	Molar %[a]	Mass %	Moles
CO (28)	10.7	7.4	$4.44\cdot10^{-2}$
H_2O (18)	16.5	7.2	$6.81\cdot10^{-2}$
2-Propanol (60)	32.8	48.1	0.1355
Propene (42)	28.7	29.5	0.1187
Isopropyl formate (88)	3.6	7.8	$1.49\cdot10^{-2}$

[a] The difference from 100% of the sum of these percentage values is correlate to the intrinsic error attributable to this procedure; i.e. 7.7%

On the other hand, by hypothesizing that the 34.0 mg of residual solid, recovered after the pyrolysis process up to 1000°C, consist of a pure TiO_2 matrix, a 0.4257 mmol of TiO_2 were calculated. Consequently, the same amount of Ti atoms may be present in the initial TiO_2 gel. By taking into account the reactions above proposed to justify the release of H_2O (Eq. (1)), 2-propanol (Eq. (2)), isopropyl formate (Eq. (3)), propene (Eq. (4)), CO (Eq. (5)), and their evolved quantities, the moles of isopropoxide, hydroxyl and formate groups originally bonded to the titanium atoms in the TiO_2 network are 0.269, 0.272 and 0.0593 mmol, respectively. From the difference between the 1.7028 mmol of bonds to titanium atoms and the 0.6001 mmol of bonds with the above terminal groups, 1.1027 mmol of bridging oxygen bonds are calculated. This gel composition, described by a nominal formula

$$TiO_{1.30}(OH)_{0.64}(OCH(CH_3)_2)_{0.61}(OCOH)_{0.14},$$

leads to a mass balance of 20.4 mg of Ti atoms, 15.9 mg of $–O–CH(CH_3)_2$ groups, 2.7 mg of –O–COH, 4.6 mg of –OH and 8.8 mg of bridging oxygen atoms, for a total 52.4 mg of gel in comparison with the experimental 50.9 mg. This satisfactory result (relative error +3%) confirms the validity of the proposed reactions to describe the gel-network rearrangements during the pyrolysis process, together with the qualitative and quantitative identification of the evolved gas mixture. This error could be further reduced by taking into account that a small fraction of released water and 2-propanol molecules can be originally adsorbed or entrapped inside the gel structure.

Conclusions

The sol–gel method allows the easy preparation of amorphous TiO_2-gels with high specific surface area, which yield polycrystalline TiO_2-anatase powders at temperatures close to 420°C for subsequent thermal treatments, as shown by DTA analyses and XRD spectra. The pyrolysis study, carried out by coupling TG-MS and TG-GC-MS analyses, allows a detailed description of reactions involving TiO_2 network rearrangement, due to the release of TiO_2-gel organic moiety. Actually, the incomplete hydrolysis of titanium alkoxide precursor, although carried out under strongly acidic medium, leaves in the TiO_2 matrix isopropoxide groups. The last are released at lower temperatures (70–230°C) as 2-propanol by reaction with residual ≡Ti–OH groups, whereas at higher temperatures (190–260°C) evolution of propene and formation of new ≡Ti–OH groups by elimination reaction occurred. A gel of high specific surface area characterized by the presence of high residual organic species is obtained by using formic acid as chelating agent in order to control the hydrolysis of $Ti(OCH(CH_3)_2)_4$. The pyrolysis of formate group involves, at lower temperatures (120–170°C), the release of isopropyl formate by reaction with isopropoxide groups, whereas at higher temperatures (200–280°C) the direct evolution of CO by elimination reaction.

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