Journal of Thermal Analysis and Calorimetry, Vol. 81 (2005) 407–415

PYROLYSIS STUDY OF SOL–GEL DERIVED ZIRCONIA BY TG-GC-MS

P. Egger, S. Dirè, M. Ischia and R. Campostrini[*]

Dipartimento di Ingegneria dei Materiali e Tecnologie Industriali, Università di Trento, via Mesiano 77, 38050 Trento, Italy

A homogeneous ZrO_2 gel was obtained by hydrolysis-condensation of zirconium(IV) *n*-propoxide previously reacted with acetic acid. Dried zirconia powders were characterized by Fourier transformed infra-red (FTIR) and X-ray diffraction (XRD) analyses. Thermogravimetric (TG) and differential thermal analysis (DTA) coupled with mass spectrometric (MS) and gas chromatographic (GC) measurements were carried out in order to identify and quantify the organic products released during the ZrO_2 gel pyrolysis. The TG-MS semi-quantitative analysis of the main released species allowed to describe the chemical rearrangement occurring in the solid during heating and to determine the chemical composition of the initial gel.

Keywords: *pyrolysis study, sol–gel synthesis, thermogravimetric-mass spectrometric coupled analyses,* ZrO_2

Introduction

Nowadays, zirconia is considered an important material of technological interest due to the exceptional properties, which lead to its use in many application fields. Zirconia-based ceramics are widely employed as optical, electronic and conductive materials [1, 2], thermal barriers [3–6], wear resistant materials [7, 8], high temperature catalysts and membranes [9], and for the preparation of ceramic tools [10–12]. Moreover, doping with other elements such as yttrium offers the possibility to stabilize the cubic ZrO_2 polymorph and to increase the ionic conductivity. Yttria-stabilized zirconia (YSZ) is generally known as one of the most suitable materials for the preparation of the solid electrolyte in solid oxide fuel cells (SOFC) [13].

The sol–gel process is often used to prepare ZrO_2-based materials because it allows to govern structure-property relationships, microstructure and phase transformation by controlling the synthesis conditions during the hydrolysis-condensation reactions of metal oxide precursors [14]. The complexation of transition metal alkoxides with organic ligands before the hydrolysis-condensation reaction is commonly used in order to obtain homogeneous gels [15]. This synthesis procedure usually leads to the incomplete removal of coordinated organics by hydrolysis, and affects gel composition and degree of cross-linking. The residual organic fraction is lost during the heat treatment performed to obtain the final ceramic material, thus affecting the microstructure and the crystallization process.

During the gel pyrolysis, the undesired phenomenon of cracks formation inhibits the preparation of bulk ceramic materials particularly in the case of transition metal oxides [14]. An effective way to avoid crack formation was recently proposed by Kozuka *et al*. [16], based on the addition of an organic polymer acting as stress relaxing agent during the heat treatment. Some of us have recently reported the preparation of YSZ freestanding thick ceramic films obtained by pyrolysis of hybrid polyvinylpyrrolidone–yttria–zirconia gels [17]. The polymer-to-ceramic transformation was shown to depend on the amount and molecular mass of the polymer, according to the DTA-TG study, and to affect the microstructural features of the final ceramics. With the aim to clarify the influence of the polymer on the thermal conversion of these organic-inorganic hybrid materials, a preliminary study on the pyrolysis of pure ZrO_2 and YSZ samples prepared by the same experimental procedure without polymer addition was undertaken. We present here the pyrolysis study of a zirconia xerogel prepared by hydrolysis-condensation of zirconium *n*-propoxide reacted with acetic acid in *n*-propanol solution. The semiquantitative analysis of the evolved gas phase during the pyrolysis by means of coupled thermogravimetric, gas chromatographic and mass spectrometric analysis allows to obtain information on the chemical rearrangements occurring in the inorganic matrix during heating and to calculate the chemical composition of the starting ZrO_2 xerogel.

Experimental

Chemicals

Zirconium(IV) *n*-propoxide (70 mass% in 1-propanol solution) was purchased from ABCR, acetic acid

---

[*] Author for correspondence: renzo.campostrini@ing.unitn.it

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary

Springer, Dordrecht, The Netherlands

(99.7%) and 1-propanol (99.5%) were Aldrich products. These reagent grade chemicals were used as received without any further purification.

Instrumentation

FTIR spectra were recorded on a Nicolet Magna 550 FTIR spectrometer in transmission mode in the 4000–400 cm^{-1} range. Powdered samples were analyzed in KBr pellets, by collecting and averaging 64 scans with 4 cm^{-1} resolution.

XRD spectra were collected on a Rigaku Dmax diffractometer in the Bragg–Brentano configuration, using CuK_α radiation and a monochromator on the diffracted beam, operating at 40 kV and 30 mA. Powdered samples were analysed by step scanning, by measuring the intensity data in the 10–110° 2θ range, with 2θ step size of 0.05° and acquisition time of 8 s per point. A modified Rietveld method analysis [18] was employed for phase analysis and mean crystallite size calculation.

Thermogravimetric and differential thermal analyses were performed on a LabSys Setaram thermobalance. Thermal analyses were carried out in the range 20–1000°C, with a heating rate of 10 K min^{-1}, by working under 100 cm^3 min^{-1} He flow. Powdered samples (20–40 mg) were analysed in 100 nm^3 alumina crucible by using 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 by using an OV1 capillary column (25 m, 0.32 mm), He as carrier gas (20 kPa inlet pressure) with temperature program: 30°C for 5 min followed by 5 K min^{-1} heating up to 200°C. Gas phase sampling (injection of 100 nm^3) was performed by means of a GR8 Bimatic micro-valve thermostatted at 130°C.

The mass spectra analysis was carried out by using VG-QMD-1000 Carlo Erba Instruments quadrupole mass spectrometer. Electron impact mass spectra (70 eV) were continuously recorded with frequency 1 scan s^{-1} in the 3–500 amu range.

TG-MS and TG-GC-MS coupled measurements

The pyrolysis study was realized by using two types of home-assembled interfaces described in the details elsewhere [19]. In TG-MS measurements any species released in gas phase from the solid sample during the thermogravimetric analysis was directly transferred and detected by the mass spectrometer by means of an appropriate capillary column transfer line. In TG-GC-MS interface the gas phase injection, containing species contemporaneously released during a specific mass loss, was resolved by means of a gas chromatographic elution, before to analyze the different compounds by mass spectrometry.

TG-MS semiquantitative data processing

The chemical composition of the dried ZrO_2-gel matrix was calculated by integrating the signals of suitable fragmentation ions of the mainly released species, following the procedure recently reported [20–23].

Synthesis of ZrO_2-gel sample

Zr-*n*-propoxide was diluted in *n*-propanol (molar ratio $n\text{-PrOH/Zr(O-}n\text{-Pr)}_4=17$). Acetic acid ($CH_3COOH/Zr(O\text{-}n\text{-Pr})_4=1$) was slowly added under vigorous stirring to the alkoxide solution at room temperature. After 30 min, distilled water ($H_2O/Zr(O\text{-}n\text{-Pr})_4=1$) was added dropwise into the yellowish solution. The initial cloudy sol turned into a transparent solution within 15 min stirring. After 4 h the solution was poured into a polypropylene vessel and aged for 2 days until gel formation. Gel sample was milled to a coarse powder, which was dried at room temperature for 5 days, then under vacuum (1.33 Pa) for 2 days, yielding the ZrO_2 xerogel specimen. The dried powder was labelled as ZrO_2-gel for the sake of conciseness.

Results and discussion

Structural and microstructural characterization of ZrO_2 sample

The FTIR spectrum of dried ZrO_2 gel, shown in Fig. 1, displays the antisymmetric and symmetric stretching vibration of the acetate groups at 1566 and 1450 cm^{-1}, respectively [24]. The strong splitting of these peaks indicates that the acetate ligands are coordinated in different ways to the Zr atoms, i.e. in unidentate, bidentate or bridging coordination modes. The intense broad band located at 3500 cm^{-1} is due to the stretching vibration of –O–H bonds. The stretching vibration of the C–O bond in the $\equiv Zr–O–CH_2CH_2CH_3$ group is detected at 1150 cm^{-1}. Typical absorption signals of zirconia gels are observed at 650 cm^{-1} attributed to $\equiv$Zr–OX (X=H, $CH_2CH_2CH_3$), and at 480 cm^{-1} due to the $\equiv$Zr–O–Zr$\equiv$ bonds [25, 26]. The FTIR spectra for the samples heated up to 500 and 800°C (Fig. 1) show only absorptions due to the zirconia network, besides small bands at 3300 and 1630 cm^{-1} of adsorbed water.

According to the XRD study (Fig. 2), the ZrO_2 xerogel is amorphous. The XRD spectrum of the sample heated at 500°C shows the crystallization of the tetragonal ZrO_2 phase (JCPDS card n° 42–1164). By heating at 800°C, the *t*-ZrO_2 crystalline reflections in-

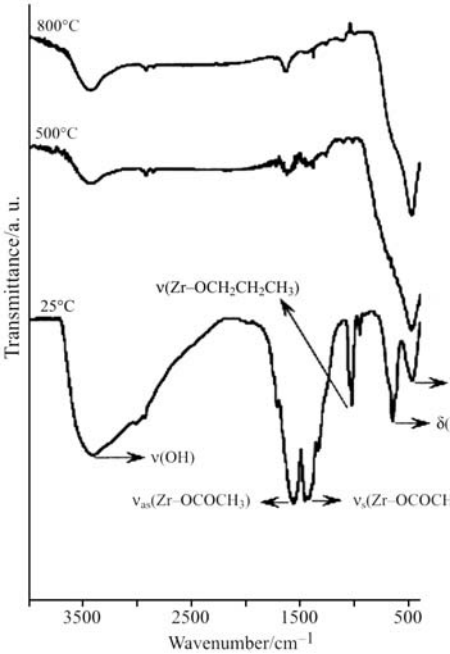

Fig. 1 FTIR spectra of ZrO_2 sample dried at room temperature and after heat treatment up to 500 and 800°C

crease in intensity and the peak line-width decreases. The results of the profile fitting procedure applied to XRD spectra are summarized in Table 1. The cell parameters are in agreement with those reported for the *t*-ZrO_2 phase. The samples present a pure nanocrystalline *t*-ZrO_2 phase with crystallite mean size increasing with temperature, and no reflections of the monoclinic zirconia polymorph are detected at 800°C. Indeed, the formation of a stable *t*-ZrO_2 phase, in the absence of stabilization with divalent or trivalent cations, requires that the crystallite mean size stays below 30 nm, approximately [27]. The spectra of the thermal treated samples also show the presence of a small signal at 2θ=15°, due to an unidentified phase; actually, this peak was detected in all our ZrO_2-based gels, nevertheless data processing allows to exclude any zirconia phase.

Thermal behaviour of ZrO_2 sample

As shown in Fig. 3 the TG analysis of dried ZrO_2 gel presents a total mass loss of 34.4% in the 75–1000°C range. The DTG curve shows an intense peak centred

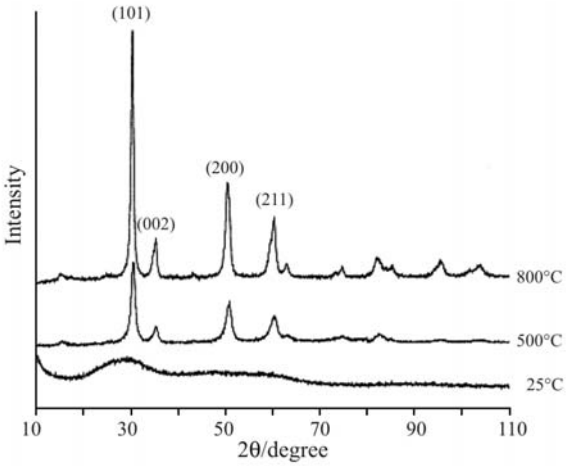

Fig. 2 X-ray diffraction analyses of ZrO_2 sample dried at room temperature and after heat treatment up to 500 and 800°C (tetragonal zirconia phase reference card JCPDS n° 42–1164)

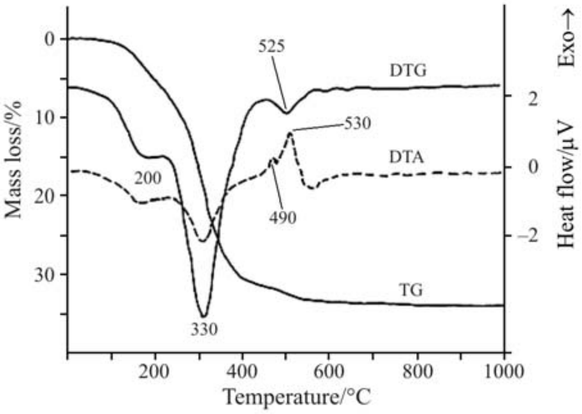

Fig. 3 Thermal analysis of dried ZrO_2 gel; TG, DTG, DTA curves *vs*. pyrolysis temperature

at 330°C, with a partially overlapped band at 200°C, followed by a second modest signal at 525°C. DTA curve displays two endothermic bands, referring to DTG events at 200 and 330°C, and two modest exothermic peaks: the former, less intense at 490°C and the latter at 530°C. These two exothermal peaks can be correlated to the crystallization process by taking into account the small corresponding DTG peak and that oxidation effects are unlikely under our experimental conditions. Table 2 summarizes the main thermal data.

Table 1 Values calculated from the Rietveld modified analysis of XRD data; (Tetragonal zirconia structure from JCPDS card n° 42–1164 gives reference values for *a* and *c* cell parameter of 0.364 and 0.527 nm, respectively)

Sample	Temperature/°C	Average crystallite size/nm	Cell parameters	
			a/nm	*c*/nm
ZrO_2	500	5.4±0.1	0.359±0.001	0.516±0.002
ZrO_2	800	10.3±0.1	0.359±0.001	0.517±0.001

In TG-MS measurement, the contribution of the evolved gas species gives a total ion current (TIC) curve obtained from the sum of all ions detected in each mass spectrum. The TIC curve of the ZrO_2 gel (Fig. 4) shows a trend closely symmetric to that of the DTG curve, confirming the correct operation of the TG-MS interface. Mass spectra, recorded in the TG-MS analysis and related with the most important thermogravimetric events, indicate the main evolution of CH_3COOH (Fig. 4, inset *T*=200°C, *m/z* signals at 43,

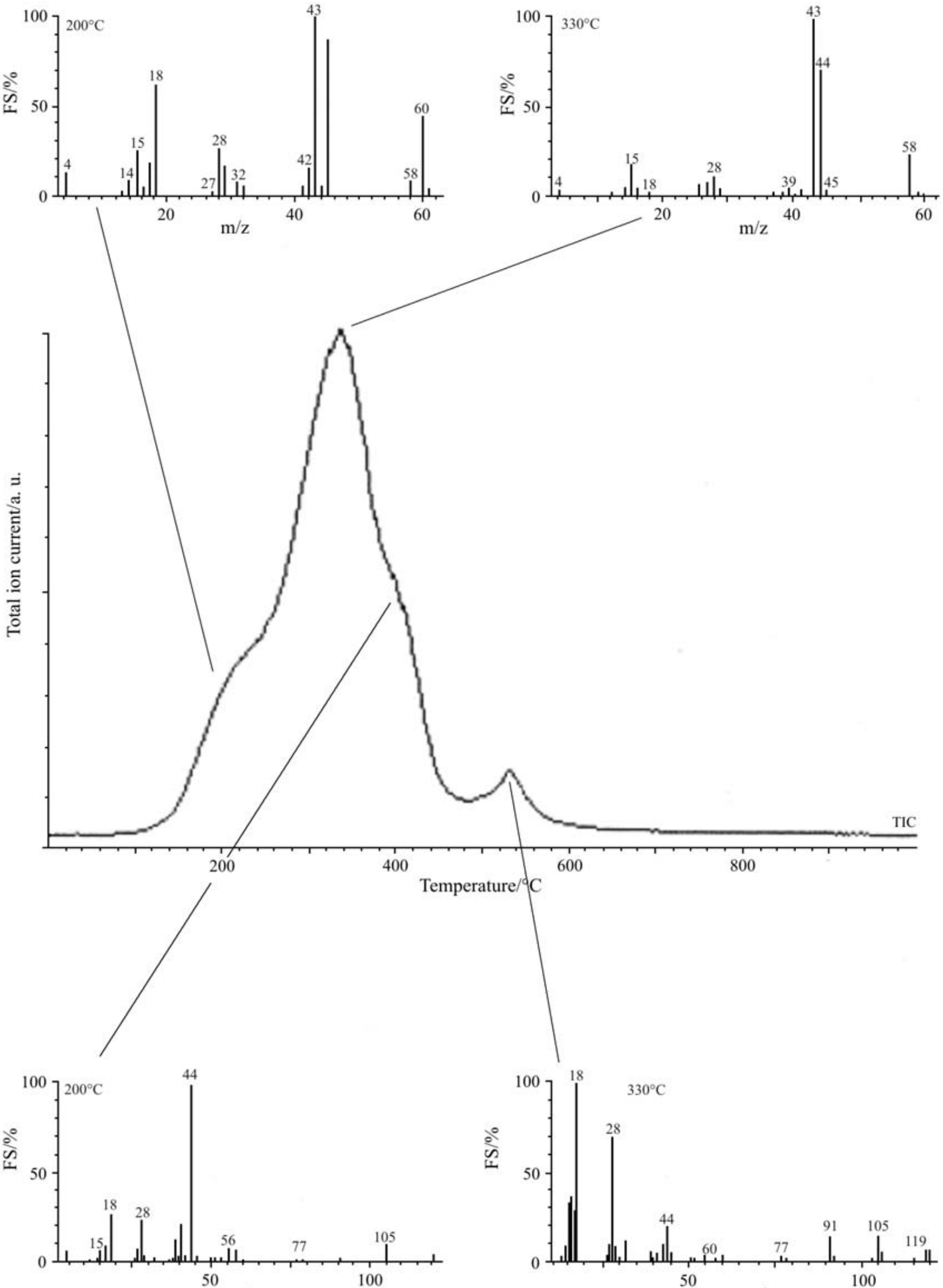

Fig. 4 Total ion current (TIC curve) of the evolved gas phase in the TG-MS analysis of the dried ZrO_2 gel. In the insets mass spectra recorded corresponding to selected pyrolysis temperatures

45, 60) and H_2O (*m*/*z* signals at 18, 17) at 200°C. These species could derive from thermally activated condensation reactions involving residual vicinal acetate and hydroxyl groups present in the ZrO_2 gel network:

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

$$\equiv\text{Zr–OH}+\text{CH}_3\text{CO–O–Zr}\equiv\rightarrow \equiv\text{Zr–O–Zr}\equiv+\text{CH}_3\text{COOH}_{(g)} \quad (2)$$

At 330°C the release of CH_3COCH_3 (Fig. 4, inset *T*=330°C, *m*/*z* signals at 43, 58) and CO_2 (*m*/*z* signal at 44) is observed. Mass spectra recorded in the shoulder of the TIC peak at *T*=400°C prove the main presence of CO_2 and a lower content of the previously detected species, and other hydrocarbons. In the TIC peak at *T*=530°C, H_2O and CO (inset *T*=530°C, *m*/*z* signal at 28) are present together with an increased amount of hydrocarbons (*m*/*z* signals at 120, 105, 91, 44, 43, 28, 27, 16, 15).

Some TG-GC-MS measurements were carried out sampling the gas phase released at the most significant temperatures in order to better identify these compounds; gas chromatographic elutions carried out at 200, 330 and 525°C are reported in Fig. 5. Table 2 reports the species detected at the different temperatures. Acetic acid together with water in lower amount are the only species released at 200°C, whereas acetone, carbon dioxide, and acetic acid in lower extent, are the compounds detected at 330°C. CH_3COCH_3 and CO_2 derive from reactions involving the migration of a methyl group between two vicinal ≡Zr–O–$COCH_3$ groups as usually observed in sol–gel metal-oxide matrices prepared from metal alkoxide precursors previously stabilized by the acetate group [28–30]:

$$2\equiv\text{Zr–OCOCH}_3\rightarrow\equiv\text{Zr–O–Zr}\equiv +\text{CH}_3\text{COCH}_{3(g)}+\text{CO}_{2(g)} \quad (3)$$

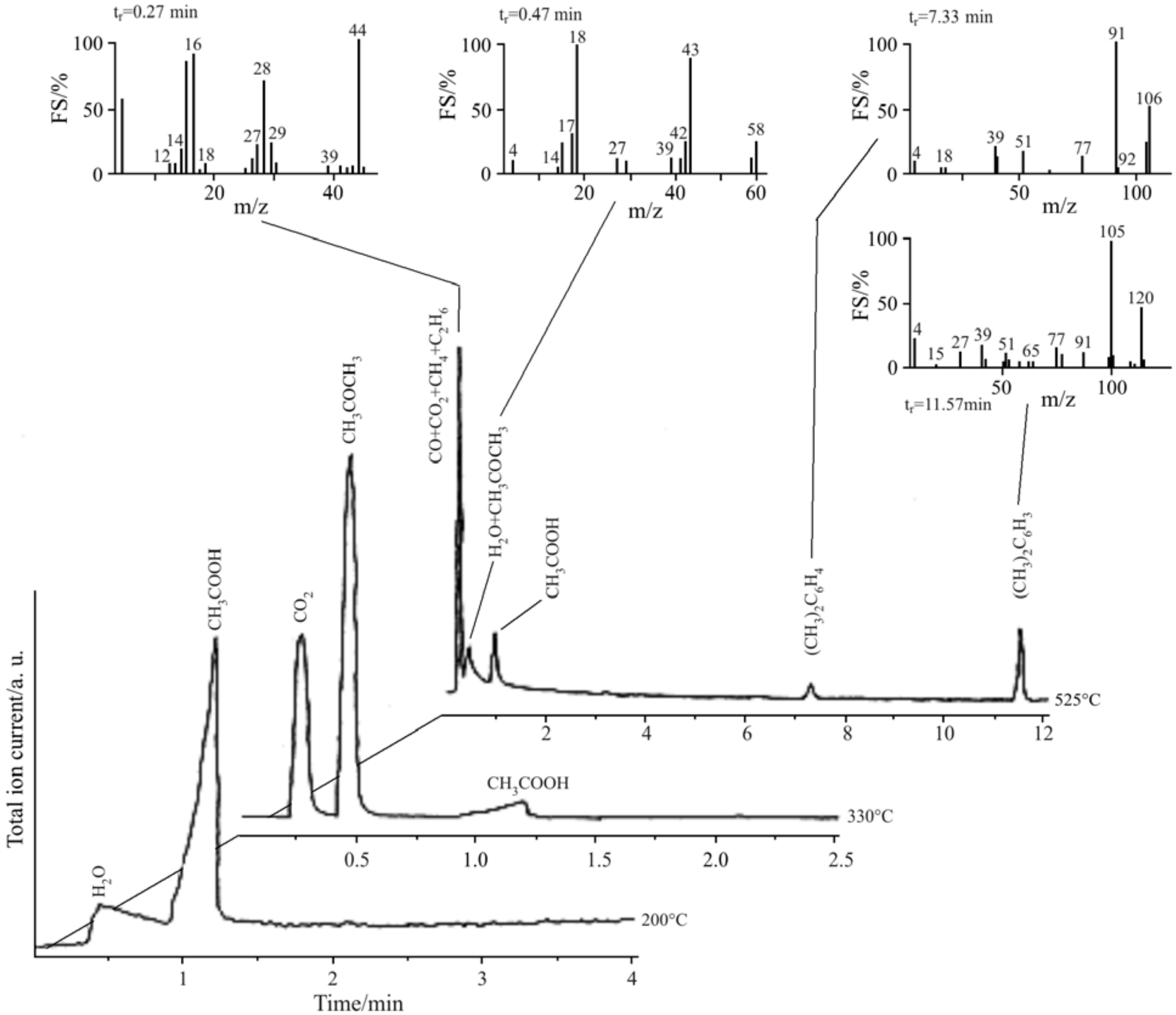

Fig. 5 Gas chromatographic elutions of the gas phase evolved at 200, 330 and 525°C in the pyrolysis of ZrO_2-gel. In the insets mass spectra recorded corresponding to selected chromatographic peaks (TG-GC-MS analyses)

Table 2 Mass losses detected in the pyrolysis of the dried ZrO_2 sample; evolved chemical species detected in the gas chromatographic elutions of TG-GC-MS analyses (100 nm^3 sampling)

Mass losses		Thermal event	*T* gas-phase sampling/°C	Identified chemical species[a,b] (intensity)[c]
T interval/°C	Relative intensity/%			
75–240	6.8	endothermic	200	H_2O (*l*), CH_3COOH (*h*)
240–470	25.1	endothermic	330	CO_2 (*h*), CH_3COCH_3 (*h*), CH_3COOH (*l*), $CH_3COOCH_2CH_2CH_3$ (*t*)
470–590	1.8	exothermic	525	[$CO+CH_4+CO_2+C_2H_6$] (*h*), [$CH_3COCH_3+H_2O$] (*l*), CH_3COOH (*l*), toluene (*t*), a dimethylbenzene isomer (*vl*), 1,3,5-trimethylbenzene (*m*)
590–1000	0.7	–	–	–

[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; *vl*=very low; *t*=traces

The gas chromatogram sampled at 525°C displays a first intense peak (retention time t_r=0.27 min) where the unresolved CO, CO_2, CH_4 and C_2H_6 species are present (mass spectra of inset t_r=0.27 min: CH_4 *m*/*z* signals at 16, 15, 14; C_2H_6 *m*/*z* signals at 30, 29, 28, 27, 26). A second unresolved small peak shows the occurrence of H_2O and CH_3COCH_3 (mass spectra of inset t_r=0.47 min), followed by a third peak due to CH_3COOH. Relevant amounts of 1,3,5-trimethylbenzene give rise to the peak at t_r=11.57 min, whereas very low amounts of a dimethylbenzene isomer lead to a small peak at t_r=7.33 min. These aromatic hydrocarbons could derive from dehydrogenation and cyclization of evolved propene, which is formed by elimination reaction of not hydrolyzed *n*-propoxide groups as observed in other studies [28–31]:

$$\equiv Zr–OCH_2CH_2CH_3 \rightarrow \equiv Zr–OH+CH_3–CH=CH_{2(g)} \quad (4)$$

$$3CH_3–CH=CH_{2(g)} \rightarrow (CH_3)_3C_6H_{3(g)}+3H_{2(g)} \quad (5)$$

Gel matrices prepared from metal *iso*-propoxide precursors usually display the evolution of the parent alcohol. On the contrary, the release of *n*-propanol was not observed during the whole pyrolysis process of this ZrO_2 sample. Moreover, even the presence of propene was not detected, suggesting that the reactions that quickly convert this species into the aromatic hydrocarbons could be catalyzed by the presence of the zirconia-oxide matrix.

During the gel pyrolysis process, the evolution of a single molecular species can be monitored by the plot of a particular *m*/*z* ion current (IC) appropriately selected among the fragmentation ion pattern of that compound. In ZrO_2 gel analysis, the main evolved species were monitored by taking into account the following *m*/*z* ion currents: *m*/*z* 18 for H_2O; *m*/*z* 60 for CH_3COOH; *m*/*z* 44 for CO_2; *m*/*z* 58 for CH_3COCH_3; *m*/*z* 120 for 1,3,5-trimethylbenzene. As shown in Fig. 6, the release of water is described by three distinct bands, centred at 190, 385 and 535°C. In particular the latter release generates the TIC peak at *T*=530°C. The evolution of acetic acid is depicted by a symmetric band centred at 250°C, which forms, together with the first water release, the shoulder of the main TIC peak at *T*=200°C. The release of carbon dioxide and acetone is shown by broader bands centred at 345 and 325°C, respectively. The evolution of these two species together leads to the intense peak at *T*=330°C in the TIC curve. Finally, the release of 1,3,5-trimethylbenzene is described by a peak at 400°C followed by a small one at 530°C. The correct description of the whole pyrolysis process is proved by the perfect overlapping of the curve obtained from the sum of the representative *m*/*z* signals of the above species and the experimental TIC curve.

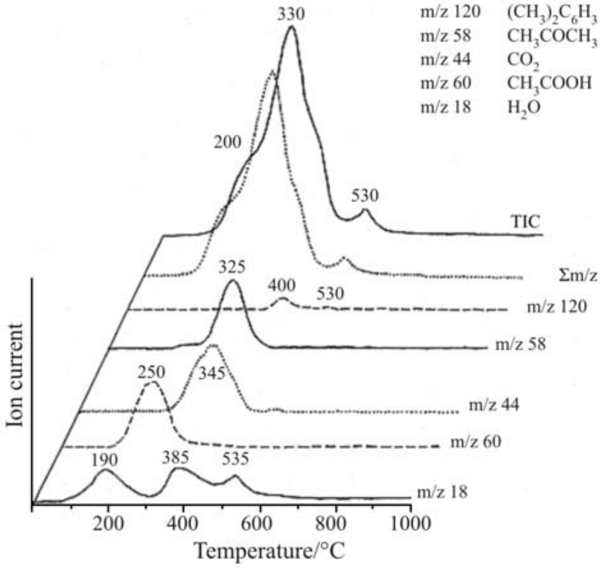

Fig. 6 Ion currents of selected ions chosen to represent the main released chemical species during ZrO_2 gel pyrolysis. The intensity of each *m*/*z* ion current is plotted considering the molar concentration value found for that compound in the TG-MS semiquantitative analysis (Table 3). Comparison between the total ion current and the sum of these ion currents

Table 3 Data from mass spectra of pure chemical species (collected in TG-GC-MS measurements) and from integrated values of *m*/*z* ion currents[a] (collected in TG-MS measurement)

Chemical species, *m*/*z* representative ion, [integrated *m*/*z* value obtained by TG-MS analysis/a. u.]	*m*/*z* ions from mass spectra of pure substance in TG-GC-MS analyses, (peak height/mm), [integrated *m*/*z* signal value/a. u.][b]	(Sum of the peak heights/mm) [integrated amount value of the chemical species/a. u.]
H_2O, 18, [$205.2701\cdot10^6$]	16 (3); 17 (23); 18 (87)	(113) [$266.6192\cdot10^6$]
CH_3COOH, 60, [$80.9227\cdot10^6$]	13 (5); 14 (11); 15 (30); 16 (4); 28 (3); 29 (13); 31 (4); 40 (3); 41 (5); 42 (16); 43 (81); 45 (87); 60 (43)	(305) [$573.9197\cdot10^6$]
CO_2, 44, [$516.0485\cdot10^6$]	12 (2); 16 (8); 28 (9); 44 (87); 45 (1)	(107) [$626.8162\cdot10^6$]
CH_3COCH_3, 58, [$122.1618\cdot10^6$]	14 (5); 15 (21); 26 (5); 27 (7); 29 (3); 37 (2); 38 (3); 39 (5); 40 (1); 41 (3) ; 42 (9); 43 (87); 44 (2) [$6.3843\cdot10^6$]; 58 (38); 59 (2)	(193) [$616.0861\cdot10^6$]
1,3,5-trimethylbenzene, 120, [$8.9697\cdot10^6$]	15 (3); 27 (9); 28 (3); 39 (16); 40 (5); 41 (7); 50 (4); 51 (11); 52 (4); 53 (4); 58 (4) [$0.8545\cdot10^6$]; 59 (3); 63 (5); 65 (6); 77 (16); 78 (5); 79 (9); 91 (12); 103 (7); 104 (1); 105 (87); 106 (8); 115 (4); 117 (2); 119 (11); 120 (42); 121 (4)	(292) [$62.3762\cdot10^6$]

[a] The integrated values are row data directly calculated by the software of the mass-spectrometer. In the data processing all the digits of the values were considered but the final parameter values (i.e.: mol% and released amount) are given with the correct number of digits, according to statistical data analysis; [b] For the sake of conciseness, only the values used in the processing data are summarized

Semi-quantitative evaluation of ZrO_2 gel pyrolysis data

On the basis of the main evolved species, their detected gas phase amounts and the reaction mechanism involved in their release, a semiquantitative interpretation of the pyrolysis process can be proposed in order to determine the chemical composition of the initial ZrO_2 xerogel [20].

The TG-MS analysis of ZrO_2 sample was carried out on 23.4 mg of dried powder yielding a residual solid of 15.4 and 8.0 mg of evolved gas. As previously described, mainly released species were: water, acetic acid, carbon dioxide, acetone, and 1,3,5-trimethylbenzene. The amount ($A(j)$) of each released species (j) was determined, first, by integrating the curve of its representative *m*/*z* ion (i) during the whole pyrolysis process ($Im/z(i)$), then, by dividing this last value by the relative intensity ($r(i)$) that this ion has inside the mass spectrum of the pure substance ($A(j)=Im/z(i)/r(i)$). In turn, when useful, the contribution of the integrated value of each ion present in the mass spectrum of that j-species can be calculated by: $Im/z(i)_j=A(j)r(i)_j$. Table 3 summarizes: (1) the relative intensity of all ions detected in the mass spectrum of each pure chemical species as recorded in the TG-GC-MS analyses ($r(i)=h(i)/\sum h(i)$, where $h(i)$ represents the height of the *m*/*z* peak in the mass spectrum of that species); (2) the integrated values of the appropriate ion currents ($Im/z(i)$), subsequently employed in the data processing; (3) the released amount of each species. Water, acetic acid and 1,3,5-trimethylbenzene amounts were directly calculated from the integrated ion currents of their representative ions, being these signals not common to the fragmentation pattern of the other evolved species. On the other hand, acetone and carbon dioxide amounts were evaluated by considering that the integrated ion currents of their representative ions include the contribution arising from other species, i.e.:

$$Im/z(58)_{\text{acetone}}=Im/z(58)_{\text{TG-MS}}-Im/z(58)_{\text{1,3,5-trimethylbenzene}}$$
$$Im/z(44)_{\text{carbon dioxide}}=Im/z(44)_{\text{TG-MS}}-Im/z(44)_{\text{acetone}}$$

From the released amount values ($A(j)$), the molar and mass percentage of each chemical species in the total evolved gas phase was calculated: $\%_{\text{mol}}(j)=100A(j)/\sum A(j)$. Subsequently, the absolute amount of each released species was deduced by considering the total mass loss of the ZrO_2 sample. Table 4 shows the chemical composition of the gas phase (8.0 mg) evolved during the whole pyrolysis process; indeed, this procedure leads to a semiquantitative analysis of the gas phase with the approximation of considering the mass spectrometer as a gas chromatographic detector having the same sensibility in revealing any different chemical compound.

According to the hypothesis that after the pyrolysis process up to 1000°C, the mass of the residual

Table 4 Chemical composition of gas mixture (8.0 mg) evolved in the whole ZrO_2 pyrolysis process calculated from TG-MS data

Chemical species, (molecular mass)	Molar/%	Mass/%	Amount/ mmol
CO_2 (44)	29.2	25.0	$4.57\cdot10^{-2}$
H_2O (18)	12.4	4.4	$1.97\cdot10^{-2}$
CH_3COCH_3 (58)	28.7	32.5	$4.50\cdot10^{-2}$
CH_3COOH (60)	26.7	31.3	$4.20\cdot10^{-2}$
1,3,5-trimethylbenzene (120)	2.9	6.8	$0.46\cdot10^{-2}$

solid (15.4 mg) is constituted of pure ZrO_2, corresponding to 0.1250 mmol of ZrO_2, the same amount of Zr atoms must be considered in the initial ZrO_2-gel sample. Taking into account the reactions proposed in the above discussion to justify the release of the main observed chemical species (Eqs (1)–(5)) and their released quantities (in moles), the moles of hydroxyl, *n*-propoxide, and acetate groups, bonded to the Zr atoms inside the initial ZrO_2 gel, were calculated by solving the equation system:

$$\begin{cases} (\equiv \mathrm{Zr-OH}) = 2(\mathrm{H_2O_{(g)}}) + 1(\mathrm{CH_3COOH_{(g)}}) - \\ -3((\mathrm{CH_3})_3\mathrm{C_6H_{3(g)}}) \\ (\equiv \mathrm{Zr-OCH_2CH_2CH_3}) = 3((\mathrm{CH_3})_3\mathrm{C_6H_{3(g)}}) \\ (\equiv \mathrm{Zr-OCOCH_3}) = 1(\mathrm{CH_3COOH_{(g)}}) + \\ +1(\mathrm{CH_3COCH_{3(g)}}) + 1(\mathrm{CO_{2(g)}}) \end{cases}$$

This stoichiometric calculus leads to 0.0676, 0.0138 and 0.1320 mmol of ≡Zr–OH, ≡Zr–$OCH_2CH_2CH_3$ and ≡Zr–$OCOCH_3$ groups, respectively. Consequently, 0.1433 mmol of bridging oxygen atoms were calculated for the residual 15.4 mg of the pyrolyzed ZrO_2 matrix from the difference between the number of Zr atom bonds and the numbers of bonds with terminal groups. From this procedure, the nominal formula $ZrO_{1.15}(OH)_{0.54}(OCH_2CH_2CH_3)_{0.11}(OCOCH_3)_{1.05}$ can be proposed in order to describe the chemical composition of the synthesized zirconia gel. The goodness of the pyrolysis process description and the relative data processing can be evaluated by the comparison between the mass value calculated for the nominal gel composition (23.4 mg) and the amount of gel employed in the experimental TG measurement (23.4 mg).

Conclusions

A homogeneous amorphous ZrO_2 sample was obtained by sol–gel method by using zirconium propoxide, previously modified by reaction with acetic acid. The gel matrix presented a high residual organic content, as proved by the remarkable total mass loss (34.4%). The thermal treatment led to the crystallization of the metal-oxide network to a single phase (tetragonal ZrO_2), yielding crystallites of 10 nm in size at 800°C as shown by XRD analyses.

A detailed pyrolysis study of the dried ZrO_2 gel was carried out by means of coupled TG-MS and TG-GC-MS measurements. The results of these analyses allowed the qualitative and semiquantitative determination of the chemical species released in the gas phase, the description of the reaction occurring during the rearrangement of the solid matrix, the determination of the chemical composition of the initial gel.

During ZrO_2 gelation, the incomplete hydrolysis of the Zr-alkoxide precursor retained in the gel matrix a relevant amount of acetate groups coordinated to the Zr atoms, together with a lower quantity of *n*-propoxide groups. Moreover, the incomplete condensation of the Zr-oligomeric units also lead to the presence of residual hydroxyl groups. During the pyrolysis process, the organic component of the ZrO_2 gel was initially released, with loss of H_2O and CH_3COOH (Eqs (1), (2)) by condensation reactions among the functional groups mainly present on the zirconium-oxide chains. After the consumption of the ≡Zr–OH groups, the remaining organic moiety underwent decomposition reactions activated by higher temperatures. The migration of methyl groups between vicinal acetate ligand led to the release of CO_2 and acetone (Eq. (3)) at about 330°C. At 400°C, the propoxide group decomposition afforded propene molecules immediately converted into aromatic hydrocarbons by means of dehydrogenation and cyclization reactions. With the completion of the organic content release during the last mass loss centred at 530°C (as confirmed by FTIR analysis), the crystallization of ZrO_2 occurred. Finally, the chemical composition of the initial gel matrix ($ZrO_{1.15}(OH)_{0.54}(OCH_2CH_2CH_3)_{0.11}(OCOCH_3)_{1.05}$) was calculated from the integration of the TG-MS signals. The reliability of the whole pyrolysis process interpretation and the chemical composition of the crude gel was also proved by the comparison between the nominal mass value derived from the proposed stoichiometric formula and the gel amount used in the experimental TG-MS measurement.

References

1 E. C. Subbarao, in Advances in Ceramics 12, Eds N. Clausen, M. Ruhle and A. H. Heuer, ACS Publ. Columbus Ohio, 1984, p. 1.

2 R. H. J. Hannink and M. V. Swain, Ann. Rev. Mater. Sci., 24 (1994) 359.

3 P. Li, I. W. Chen and J. E. Penner-Hahn, Phys. Rev., 48 (1993) 10063.

4 E. D. Wachsman, N. Jiang, C. W. Frank, D. M. Mason and D. A. Stevenson, Appl. Phys. A, 50 (1990) 545.

5 M. Brown, S. Primdahl and M. Mogensen, J. Electrochem. Soc., 147 (2000) 475.

6 R. N. Basu, C. A. Randall and M. J. Mayo, J. Am. Ceram. Soc., 84 (2001) 33.

7 H. Gasthuber, Technical report Daimler Benz AG, Stuttgart 1985.

8 G. De, A. Chatterjee and D. Ganguli, J. Mater. Sci. Lett., 9 (1990) 845.

9 S. W. Lee, S. M. Hsu and M. C. Shen, J. Am. Ceram. Soc., 76 (1993) 1937.

10 R. R. Bhave, Inorganic Membranes, Synthesis, Characterization and Properties, Van Rostrnd Reinhold Publ., New York 1991.
11 H. P. Hsieh, Inorganic Membranes, A. I. Ch. E. Symp. Ser., 84 (1998) 1.
12 P. Fornasiero, J. Kaspar and M. Graziani, Appl. Catal. B: Environmental, 22 (1999) L11.
13 S. C. Singhal, MRS Bull., 25 (2000) 16.
14 C. J. Brinker and G. W. Scherer, Sol-gel Science, Academic Press, San Diego 1990
15 J. Livage and C. Sanchez, J. Non-Cryst. Solids, 145 (1992) 11.
16 H. Kozuka, M. Kajimura, T. Hirano and K. Katayama, J. Sol-Gel Sci. Technol., 19 (2000) 205.
17 P. Egger, G. D. Sorarù and S. Dirè, J. Eur. Ceram. Soc., 24 (2004) 1371.
18 L. Lutterotti, R. Ceccato, R. Dal Maschio and E. Pagani, Mater. Sci. Forum, 278–281 (1998) 87.
19 R. Campostrini, G. D'Andrea, G. Carturan, R. Ceccato and G. D. Sorarù, J. Mater. Chem., 6 (1996) 585.
20 R. Campostrini, M. Ischia and L. Palmisano, J. Therm. Anal. Cal., 71 (2003) 997.
21 R. Campostrini, M. Ischia and L. Palmisano, J. Therm. Anal. Cal., 71 (2003) 1011.
22 R. Campostrini, M. Ischia and L. Palmisano, J. Therm. Anal. Cal., 75 (2004) 13.
23 R. Campostrini, M. Ischia and L. Palmisano, J. Therm. Anal. Cal., 75 (2004) 25.
24 J. E. Tackett, Appl. Spectrosc., 43 (1989) 483.
25 M. Jansen and E. Guenther, Chem. Mater., 7 (1995) 2110.
26 C. Guermeur, J. Lambard, J. F. Gerard and C. Sanchez, J. Mater. Chem., 9 (1999) 769.
27 R. C. Garvie, J. Phys. Chem., 69 (1965) 1238.
28 G. Marcì, L. Palmisano, A. Sclafani, A. M. Venezia, R. Campostrini, G. Carturan, C. Martin, V. Rives and G. Solana, J. Chem. Soc., Faraday Trans., 92 (1996) 819.
29 R. Di Maggio, R. Campostrini and G. Guella, Chem. Mater., 10 (1998) 3839.
30 G. Facchin, G. Carturan, R. Campostrini, S. Gialanella, L. Lutterotti, L. Armelao, G. Marcì, L. Palmisano and A. Sclafani, J. Sol-Gel Sci. Techn., 18 (2000) 29.
31 R. Campostrini, M. Ischia, G. Carturan, S. Gialanella and L. Armelao, J. Sol-Gel Sci. Techn., 18 (2000) 61.

Received: November 30, 2004
In revised form: March 23, 2005

DOI: 10.1007/s10973-005-6553-7