Non-hydrolytic sol–gel process: zirconium titanate gels

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The effectiveness of a non-hydrolytic sol–gel process for the preparation of bicomponent oxides has been studied in the 1 : 1 system TiO_2–ZrO_2. Elemental analysis by energy dispersive X-ray analysis (EDXA) and by inductively coupled plasma (ICP) showed the same Ti : Zr ratio for the amorphous oxide and crystalline $ZrTiO_4$ which corresponds to that of the initial solution. The direct crystallization of $ZrTiO_4$ below 700 °C without the intermediate formation of TiO_2 or ZrO_2 indicates that the non-hydrolytic sol–gel process gives rise to the formation of homogeneous zirconium titanate gels.

During the last decade, there has been an enormous growth of interest in chemical-based processes in materials science, owing to the potential advantages of chemical routes compared with traditional glass melting or ceramic powder methods: higher purity and homogeneity, processability and lower processing temperatures. Sol–gel processes are chemical routes for the preparation of oxide ceramics,[1–3] which have been studied extensively for the preparation of multicomponent oxides (glasses and ceramics). In these processes, based on cohydrolysis of molecular precursors such as metal alkoxides, the main problem is control of the reaction rates which are highly dependent on the nature of the metals, especially when silicon and transition metals are included in the composition.[1] To achieve homogeneous oxides with predetermined compositions, the difference in reactivity has been minimized by controlled prehydrolysis of the less reactive precursor or by chemical modification of the precursors.[2] However, research is still under way to find new chemical routes, not including sophisticated procedures, to homogeneous multicomponent material.[4]

In this context, we are developing a chemical route, which does not involve hydrolysis, for the preparation of binary oxides. As reported previously, this process is based on the thermal condensation reaction between metal chlorides and metal alkoxides (Scheme 1) or, alternatively, on the etherolysis of metal chlorides (the alkoxide functions being formed *in situ*, Scheme 2).[4–11]

$$MCl_n + M(OR)_n \rightarrow 2\ MO_{n/2} + nRCl$$

Scheme 1

$$\equiv MCl + R{-}O{-}R \rightarrow \equiv MOR + RCl$$
$$MCl_n + n/2\ R{-}O{-}R \rightarrow MO_{n/2} + nRCl$$

Scheme 2

In this way, we have prepared silica,[5] alumina[5,6,8,10] and transition-metal oxides[5,7,10] gels, as well as binary oxides in the systems Al_2O_3–SiO_2,[5,9] TiO_2–SiO_2[11] and ZrO_2–SiO_2.[11] These systems were chosen because ^{29}Si NMR spectroscopy is a tool of choice for determining the homogeneity of silicate compounds at the atomic level.[12]

When metal chlorides and metal alkoxides are mixed, fast ligand-exchange reactions occur, giving rise to a mixture of metal chloroalkoxides (Scheme 3),[8,13] so that homo- as well as hetero-condensations may occur.

$$MCl_n + M'(OR)_n \rightleftharpoons MCl_{n-x}(OR)_x + M'Cl_x(OR)_{n-x}$$

Scheme 3

Homogeneity will be achieved only if both condensations take place at similar rates. By ^{29}Si NMR studies we have shown that silica–alumina[8] and silica–zirconia[11] non-hydrolytic gels are homogeneous (*i.e.* constituted by a random mixture of Si—O—M and Si—O—Si bonds). However, silica–titania gels are not homogeneous, only about 9 mol of titania being homogeneously incorporated into the silica network.[11] The direct crystallization at low temperature of a definite compound without phase separation has also been used to determine the homogeneity of a gel, particularly when no NMR-sensitive nuclei are present in the composition. Indeed, homogeneous silica–alumina gels, in the mullite composition, crystallize directly at low temperature into tetragonal mullite (980 °C).[8] However, non-hydrolytic silica–zirconia gels with the zircon composition, shown by ^{29}Si NMR results to be homogeneous, do not crystallize directly to zircon.[11] This result shows that, while the direct crystallisation of a definite compound is a proof of homogeneity of the gel, the reverse does not necessarily result from heterogeneous gels.

To extend our study on the non-hydrolytic sol–gel route to the preparation of bicomponent oxides in which the two metals are transition metals, we have chosen to prepare gels with the composition of zirconium titanate. Indeed, $ZrTiO_4$ fulfils the necessary conditions for determination of the homogeneity of the gel precursor from its crystallization behaviour. It is a stable compound at low temperature in the phase diagram of TiO_2–ZrO_2, which has been prepared already by sol–gel processes.[14–19] When a high homogeneity level is not achieved, crystallization of TiO_2 is observed before crystallization into $ZrTiO_4$,[15] whereas homogeneous gels crystallize directly into $ZrTiO_4$ below 700 °C.[14,17–19] Note that the preparation of $ZrTiO_4$ by solid-state reaction from its constituent oxides in powder form requires elevated temperatures of 1200–1700 °C to form a homogeneous compound.[14] $ZrTiO_4$ is of interest for its useful dielectric properties in the microwave frequency range;[20] it has been cited as a host for the preparation of ceramic mixed-phase pigments of high thermal stability;[21] its acid–base catalytic activities in the monoxidative dehydrogenation of ethylbenzene to styrene and in the isomerization of cyclohexene oxide have been reported.[22]

In the present work, we report the preparation of non-hydrolytic zirconium titanate gels from titanium chloride and zirconium alkoxide, from titanium alkoxide and zirconium chloride and from a mixture of titanium and zirconium chloride and ethers as the oxygen donor (diethyl ether, diisopropyl ether, dipropyl ether). The degree of homogeneity of the gels thus prepared has been evaluated by X-ray spectral microanalysis using an EDXA spectrometer, and in terms of the crystallization behaviour.

Experimental

Starting materials

Zirconium tetrachloride (Jansen), zirconium ethoxide (Lancaster), titanium isopropoxide (Jansen) and titanium tetrachloride (Aldrich) were used as received; diisopropyl ether, dipropyl ether and diethyl ether (received from Aldrich) were distilled over sodium–benzophenone before use; dichloromethane and chloroform were distilled over P_2O_5.

Preparation of samples

The preparation of samples was carried out under argon in oven-dried glassware. One equivalent of the titanium compound [$Ti(OPr^i)_4$ or $TiCl_4$] was added to one equivalent of the zirconium compound [$ZrCl_4$ or $Zr(OEt)_4$] dissolved in chloroform or dichloromethane. When ethers were used as oxygen donors, four equivalents of the ether diluted in chloroform were added to the equimolar mixture of $TiCl_4$ and $ZrCl_4$. The mixture was stirred to complete dissolution and the solution was transferred into a tube which was then sealed. The tube was heated at 110 °C in the oven until gelation occurred. The tubes were opened in a glove-bag under argon. The solid and liquid phases were separated by filtering. The isolated gel was washed with successive aliquots of chloroform and dried under vacuum at room temperature. At this stage monolithic gels were transformed to fine powders. The powders were then dried under vacuum at 110 °C for 3 h.

Characterization techniques

Thermogravimetry and differential thermal analyses were performed in a 20:80 oxygen–nitrogen mixture, on a Netzsch STA 409 thermobalance using a heating rate of 10 K min^{-1}.

Specific surface areas were determined by the Brunauer–Emmett–Teller (BET) method using N_2 adsorption–desorption isotherms recorded on a Micromeretics ASAP 2400 analyser.

X-Ray powder diffraction patterns were recorded with Cu-Kα radiation using a Siefert MZ IV diffractometer.

The syneresis liquids were analysed by ^1H NMR spectroscopy (on a Bruker AW apparatus at 80 MHz) and gas chromatography.

Elemental analyses were performed by the Service Central d'Analyses du CNRS, France. Titanium and zirconium contents were determined by inductively coupled plasma (ICP) from an aqueous solution. Carbon and hydrogen contents were established by high-temperature combustion and IR spectroscopy. Chlorine contents were measured by potentiometric titration. Oxygen contents were calculated by difference.

On calcined samples, the Ti and Zr contents were also determined on carbon-coated powders using an energy dispersive X-ray analyser (Link AN 1000) fitted to a Cambridge Stereoscan 360 SEM (25 kV acceleration potential, 33.0° take-off angle, 7.5 mm thick Be window).

Raman spectra of powders in capillary tubes were registered with a triple monochromator spectrometer (Dilcor RT 30) using the 488 nm Ar^+ excitation line.

Results

Preparation of zirconium titanate gels

Five gel samples were prepared. In the first two, the metal chloride was mixed with the metal alkoxide dissolved in chloroform or dichloromethane; in the others, the two metal chlorides were dissolved in a mixture of $CHCl_3$ and an ether which acts as an oxygen donor (Table 1). All the mixtures were homogeneous. White opaque monolithic gels were obtained after heating the mixture at 110 °C under autogeneous pressure. The parent alkyl chloride was identified in the syneresis liquid by ^1H NMR spectroscopy and gas chromatography. When dipropyl ether ($Pr^n{}_2O$) was used as the oxygen donor, isopropyl chloride (Pr^iCl) and *n*-propylchloride (Pr^nCl) formed in a 50:50 ratio. However, when the same reaction was performed at atmospheric pressure and the alkyl chloride was distilled off as formed, the $Pr^iCl:Pr^nCl$ ratio decreased to 20:80.

The degrees of condensation of the gels were evaluated from elemental analysis of the dried gels [110 °C in vacuum for 3 h (Table 2)]. The compositions of the gels were determined assuming that carbon is present as residual alkoxide groups and that the bridging oxygen content may be calculated, knowing the chloride content, by taking into account the valence of the metal atoms. The degree of condensation was calculated as the ratio of the experimental amount of bridging oxygen to the theoretical value for the oxides. For example, for a composition of xerogel $TiZr_xCl_y(OR)_zO_m$, $m=[4(1+x)-(y+z)]/2$ and the degree of condensation (%) is $[m/2(1+x)]100$.

Table 1 Preparation of zirconium titanate gels (110 °C in sealed tubes)

gel	precursors (ratio in mmol)	solvent (metal concentration/mol dm^{-3})	gel time/h	alkyl chloride formed
1	$TiCl_4$–$Zr(OEt)_4$ (8.06:8.10)	CH_2Cl_2 ([Ti] = 1.32, [Zr] = 1.33)	<36	EtCl
2	$Ti(OPr^i)_4$–$ZrCl_4$ (15.1:14.6)	$CHCl_3$ ([Ti] = 1.11, [Zr] = 1.07)	<10	Pr^iCl
3	$TiCl_4$–$ZrCl_4$–Et_2O (21.1:19.4:78.0)	$CHCl_3$ ([Ti] = 2.04, [Zr] = 1.87)	<10	EtCl
4	$TiCl_4$–$ZrCl_4$–$Pr_2{}^iO$ (11.7:11.7:47.0)	$CHCl_3$ ([Ti] = 2.44, [Zr] = 2.44)	<10	Pr^iCl
5	$TiCl_4$–$ZrCl_4$–$Pr_2{}^nO$ (17.0:17.5:64.4)	$CHCl_3$ ([Ti] = 1.28, [Zr] = 1.32)	<36	Pr^iCl–Pr^nCl (50:50)

Table 2 Chemical analysis and degree of condensation of the dried gels (3 h, 110 °C in vacuum)

	chemical analysis (%)						
gel	C	H	Cl	Ti	Zr	composition of dried gels	D.C.[a] (%)
1	3.76	2.66	16.10	16.10	26.45	$TiZr_{0.86}Cl_{1.35}(OEt)_{0.46}O_{2.82}$	76
2	13.18	3.29	14.12	14.55	26.10	$TiZr_{0.94}Cl_{1.31}(OPr^i)_{1.2}O_{2.62}$	68
3	7.24	2.46	16.77	16.60	27.50	$TiZr_{0.87}Cl_{1.36}(OEt)_{0.87}O_{2.62}$	70
4	7.64	2.73	13.43	16.25	27.00	$TiZr_{0.87}Cl_{1.12}(OPr^i)_{0.62}O_{2.87}$	77
5	16.37	3.69	18.61	11.25	21.70	$TiZr_{1.01}Cl_{2.23}(OPr^i)_{1.94}O_{1.94}$	52

[a] Degree of condensation.

Thermal analysis of zirconium titanate gels

The thermal behaviour of the zirconium titanate gels is described in Table 3. Typical thermogravimetry (TG) and differential thermal analyses (DTA) in air, performed on gel **2** prepared from $Ti(OPr^i)_4$ and $ZrCl_4$ are shown in Fig. 1. A mass loss of 34% occurred between 150 and 500 °C, with a broad exothermic peak due to the thermal decomposition of the isopropoxide groups and the oxidation of residual groups.[10] A second sharper exothermic peak appears at around 700 °C with no mass loss. This exotherm is associated with the crystallization of $ZrTiO_4$ as shown by the X-ray diffraction patterns (Fig. 2).

For the five gels, thermal degradation occurs in the same temperature range. The mass losses (Table 3) vary from 29 to 38% as a function of the degree of condensation of the gels and the nature of the OR group ($Pr^iO > EtO$). No significant change results from the nature of oxygen donor alkoxide or ether (compare gels **1** with **3** and **2** with **4**). The mass loss owing to the transformation of the xerogel to oxide has been calculated from the composition of the xerogel (Table 3). Some discrepancies between the calculated and the experimental values may be attributed to the adsorption of moisture before analyses. The yields of zirconium titanate, calculated after calcination up to 1200 °C, were rather good, varying from 67 to 100%. The temperature of crystallization, determined from the DTA curves, changes from 660 to 690 °C with the different precursors used (Fig. 3). Note that crystallization, determined under the same conditions, appears at 705 °C for gels prepared by hydrolysis of metal alkoxides,[17] at 640 °C for products obtained from metal chlorides[15] and at 500 °C for the gel obtained from a mixture of sols, the last value being the lowest temperature reported.[19]

The specific surface areas of gels calcined at 600 °C depends strongly on the precursors and change from 13 to 126 $m^2\ g^{-1}$, the higher area surface being obtained with OPr^i groups (gels **2** and **4**), the lower with OEt groups (gels **1** and **3**). Surface areas of 55.6 and 33.1 $m^2\ g^{-1}$ have been reported previously for $ZrTiO_4$ gels prepared from sols.[19]

X-Ray diffraction analysis

The X-ray diffraction patterns reported in Fig. 2 show that after calcination at 600 °C for 4 h, gels **2**, **4** and **5** are amorphous, whereas crystallization of $ZrTiO_4$ begins to occur for gels **1** and **3**. No lines corresponding to anatase or ZrO_2 can be detected. After calcination at 750 °C crystallization of $ZrTiO_4$ is observed in all cases.

Raman spectroscopy

Raman spectroscopy is a technique more sensitive to short-range order than X-ray diffraction, and it may show the intermediate crystallization of anatase or rutile, as well as monoclinic zirconia before that of $TiZrO_4$.

Fig. 4 shows the Raman spectra of sample **2** heated at 600, 750 and 1350 °C. At 600 °C, the spectrum does not show any bands corresponding to crystalline anatase (143, 393, 512, 636 cm^{-1}), rutile (143, 236, 446, 614, 826 cm^{-1}) or monoclinic zirconia (180, 192, 476, 559, 638 cm^{-1}).[23] The 283, 331, 418,

Table 3 Thermal analyses, pore volumes, average pore sizes and surface area of zirconium titanate gels

gel	Δ *m*/*m* (calc) (%)	Δ*m*/*m* (found)[a] (%)	yield (%)	crystallization temp.[b]/°C	$V_p{}^c$/ $cm^3\ g^{-1}$	d^c/ nm	*S*/$m^2\ g^{-1}$ 600 °C	*S*/$m^2\ g^{-1}$ 750 °C
1	22	30	87.0	680	0.05	14	13	5
2	33	34	99.5	672	0.46	13	126	46
3	27	29	80.0	660	0.09	9	24	11
4	25	33	66.7	665	0.31	9	122	41
5	44	38	99.0	690	0.24	8	110	45

[a]From TG results. [b]From DTA. [c]At 600 °C.

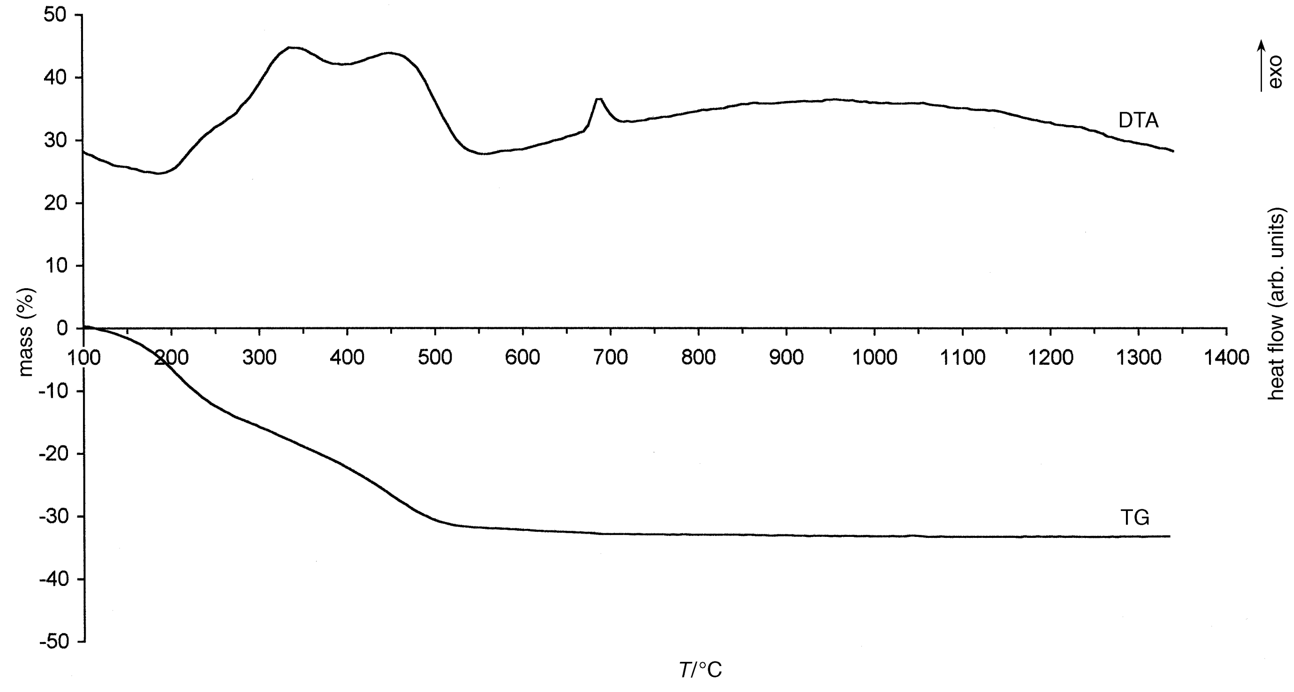


Fig. 1 TG and DTA curves of gel **2** [prepared from $Ti(OPr^i)_4$ and $ZrCl_4$]

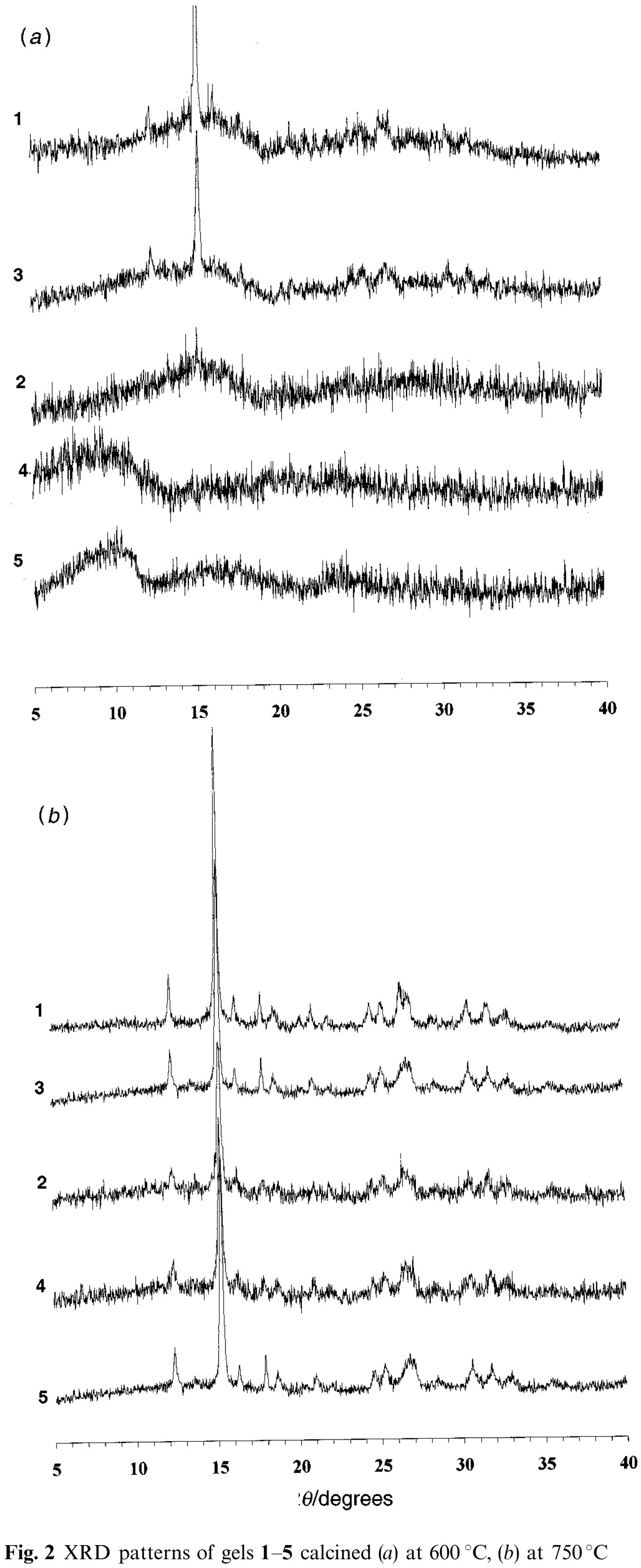


Fig. 2 XRD patterns of gels **1**–**5** calcined (*a*) at 600 °C, (*b*) at 750 °C

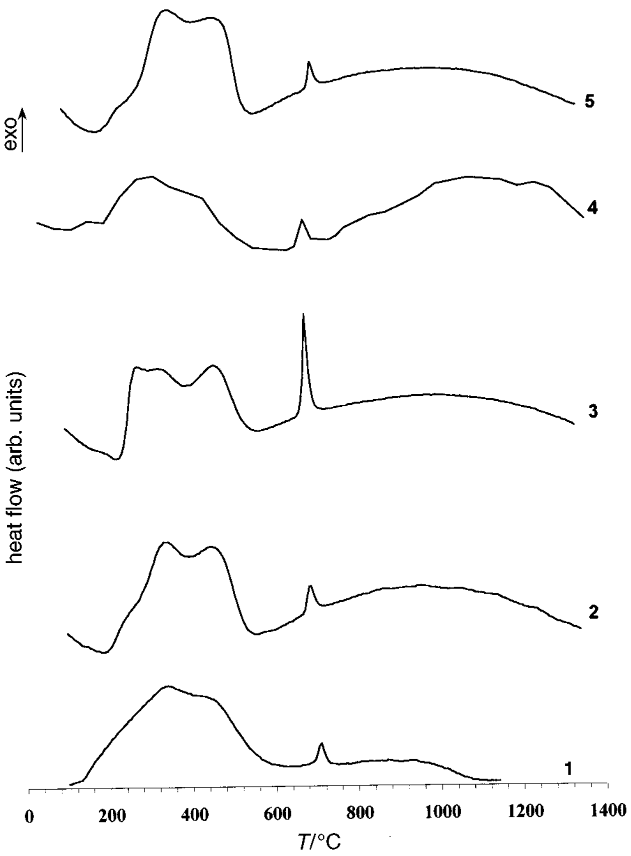


Fig. 3 DTA curves of gels **1**–**5**

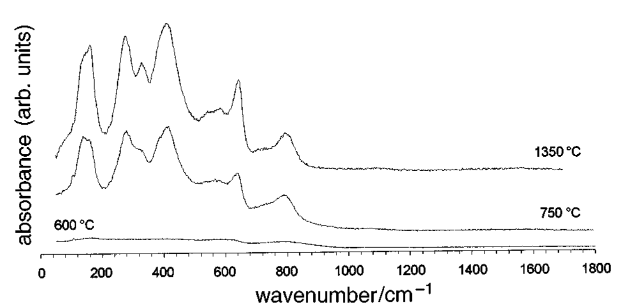


Fig. 4 Raman spectra of gel **2** calcined at 600, 750 and 1350 °C

570, 641 and 792 cm^{-1} bands observed at 750 °C may be attributed to crystalline $TiZrO_4$ as confirmed by the spectrum of the sample heated at 1350 °C.[18]

Composition of zirconium titanate samples

Table 4 shows the Ti : Zr ratio of zirconium titanate gels before and after crystallization, as determined by elemental analyses, ICP and EDXA.

The Ti : Zr ratio does not change before and after crystallization of $TiZrO_4$. The differences with the nominal ratio of the precursors are within experimental error.

Moreover, the Ti and Zr line profiles of sample **2** calcined at 600 °C (Fig. 5) show a homogeneous distribution of Ti and Zr in the powder.

As shown by SEM, samples **4** and **2** [Fig. 6(*a*) and (*b*)] calcined at 600 °C are formed from small (0.2–0.6 μm) agglomerated spherical particles. Crystallization of $ZrTiO_4$ (sample **4** heated at 750 °C) does not change the particle size [Fig. 6(*c*)]. Note that agglomerated spherical particles have been made from metal chlorides,[15] whereas unagglomerated spherical particles with particle sizes varying between 15 and 50 μm were produced from gelation of a mixed sol.[19]

Discussion

White opaque gels were obtained from solutions of metal (Ti or Zr) chloride and metal (Zr or Ti) alkoxide as well as from solutions of the two metal chlorides ($TiCl_4$, $ZrCl_4$) and ethers. The formation of alkyl chloride confirms the non-hydrolytic nature of the condensation. The use of dipropyl ether as the oxygen donor is very useful for elucidating the mechanism of condensation. Indeed, a mixture of Pr^iCl and Pr^nCl was

Table 4 Ti : Zr ratio of zirconium titanate gels (determined by elemental analyses, ICP and EDXA)

gel	precursors	Ti : Zr (nominal)	Ti : Zr at 150 °C (ICP)	Ti : Zr at 600 °C		Ti : Zr at 750 °C	
				ICP	EDX	ICP	EDX
1	$TiCl_4$–$Zr(OEt)_4$	1.00	1.16	1.12	1.12	1.15	1.12
2	$Ti(OPr^i)_4$–$ZrCl_4$	1.03	1.06	0.95	0.91		0.95
3	$TiCl_4$–$ZrCl_4$–Et_2O	1.09	1.14	1.10	0.96	1.08	0.99
4	$TiCl_4$–$ZrCl_4$–$Pr_2{}^iO$	1.00		0.88	0.92	1.00	0.91
5	$TiCl_4$–$ZrCl_4$–$Pr_2{}^nO$	0.97	0.99	0.95	0.88	0.95	0.87

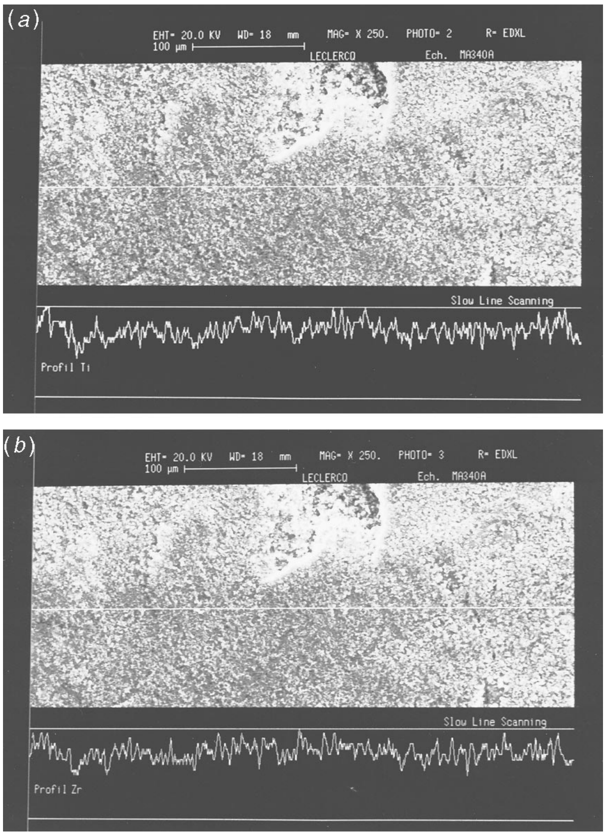


Fig. 5 Ti and Zr line profiles of gel **2** calcined at 600 °C: (*a*) Ti; (*b*) Zr

formed. The mechanism of condensation, which we have proposed previously (Scheme 4), involves a nucleophilic substitution of chloride on the carbon centre by a concerted, S_N2 or S_N1 mechanism.[4–11]

An S_N1 mechanism [pathway (3)] involves the formation of a carbocation which quickly rearranges from the primary to the more stable secondary carbocation. Thus, condensation by an S_N1 mechanism would give Pr^iCl as the major product when dipropyl ether was used. Experimentally, the $Pr^iCl : Pr^nCl$ ratio was 50 : 50 when gelation occurred in a sealed tube and 20 : 80 when the alkyl chloride was distilled off as formed.

Thus, the decrease of Pr^iCl content when the alkyl chloride is removed from the solution shows that it does not form by an S_N1 condensation mechanism, but results from isomerisation of Pr^nCl formed first. Isomerization of alkyl chloride by Lewis acids ($AlCl_3$, $FeCl_3$, $TiCl_4$, $ZrCl_4$, *etc.*) has been studied extensively, because these compounds are involved in the alkylation of aromatic rings in the Friedel–Crafts reaction.[24] The isomerisation of *n*-propyl chloride into isopropyl chloride is catalysed by the metal chlorides present in the initial solution, acting as Lewis acids. In the condensation of metal chloride and metal alkoxide, the S_N1 mechanism appears to be unlikely, at least for primary alkoxides.

The degrees of condensation of the gels formed are $>70\%$ (except in the case of $Pr^n{}_2O$), the best result (77%) being obtained with diisopropyl ether. The effectiveness of the oxygen donors in condensation decreases in the order: $Pr^i{}_2O > Zr(OEt)_4 > Et_2O > Ti(OPr^i)_4 > Pr^n{}_2O$.

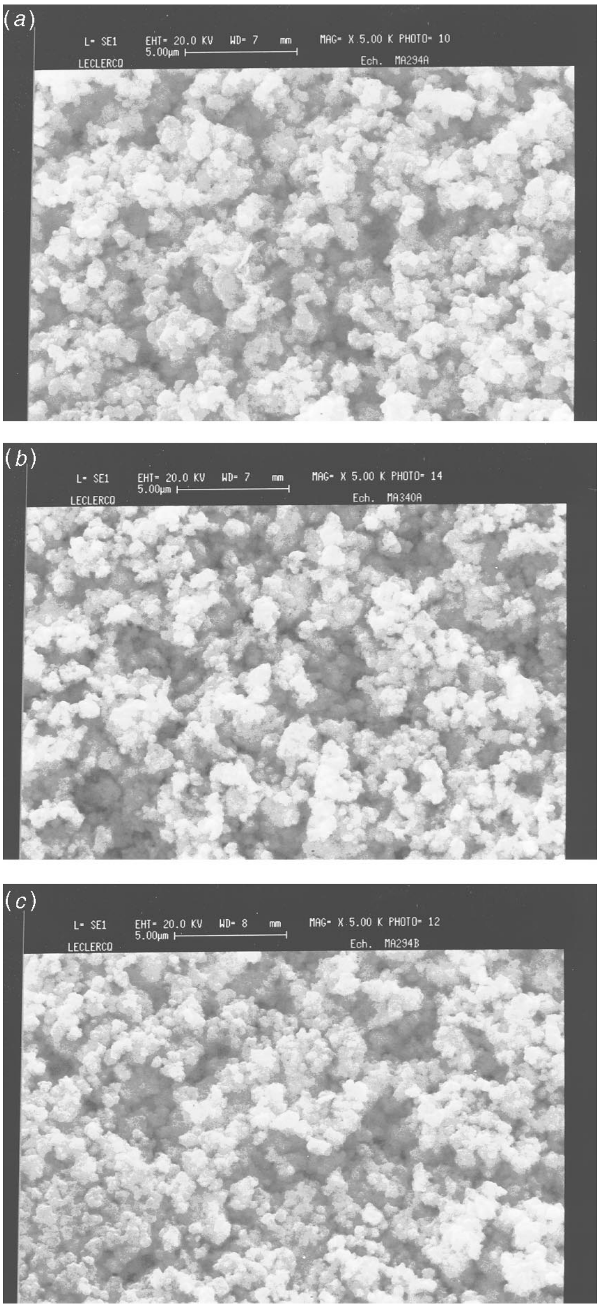
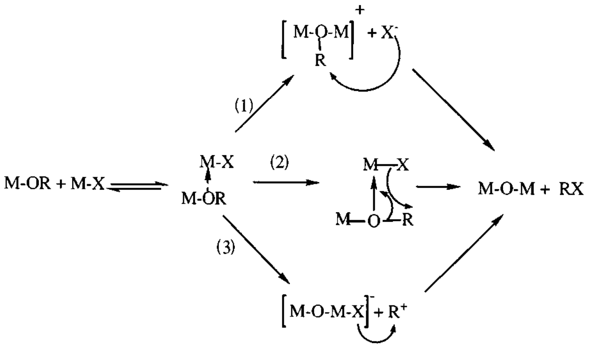


Fig. 6 SEM images of (*a*) gel **4** calcined at 600 °C, (*b*) gel **2** calcined at 600 °C, (*c*) gel **4** calcined at 750 °C

Note that even in the case of alkoxides as the oxygen donor, the amounts of alkoxide and chloride residues are not equal in dried gels. The lower content of the alkoxide residue has already been observed and attributed to its thermal decomposition during drying.[6]

TG and DTA of the dried gels show that calcination occurs



Scheme 4

between 200 and 600 °C associated with a broad exothermic peak corresponding to the thermal decomposition and the oxidation of residual organic moieties, as well as the elimination of chloride.[6] The exothermic peak near 700 °C is associated with the crystallization of $TiZrO_4$.

The Ti and Zr line profiles of samples heat-treated at 600 °C determined by EDXA indicate the same amounts of Ti and Zr throughout the sample. Furthermore, elemental analyses show the same Ti : Zr ratio in the xerogels and in the heat-treated samples, which correspond to the initial solution ratios. These results are in contrast to the behaviour of the hydroxoperoxo Zr–Ti precursor which shows different Ti : Zr ratios with the different heat-treatment temperatures, and the intermediate formation of rutile before the crystallization of $TiZrO_4$.[15] XRD and Raman spectroscopy of the non-hydrolytic samples show no intermediate formation of TiO_2. EDXA, XRD and Raman spectroscopy indicate the homogeneity of the non-hydrolytic zirconium titanate gels.

Conclusions

The non-hydrolytic process, based on the condensation reaction between metal chloride and metal alkoxide or metal chlorides and ethers, gives rise to homogeneous zirconium titanate gels. The Ti : Zr ratio remains the same throughout the process, from the solution of precursors to the crystalline sample.

The products obtained by this chemical route do not differ from those made by sol–gel processes in terms of textural features, and the temperatures of crystallization of $TiZrO_4$ correspond to those expected for a chemical route (<700 °C). Gel formation is slower than by the hydrolysis condensation processes and a higher temperature is required (110 °C *vs.* room temperature). However, the synthesis is very easy to perform; the reactants have just to be mixed and heated to give a homogeneous gel.

Furthermore, the process is versatile. A great variety of oxygen donors are effective which influence the mass loss during calcination, the textural features and the temperature of crystallization. Diisopropyl ether appears to be the most effective in term of the degree of condensation of the gel.

The non-hydrolytic process is efficient for the preparation of homogeneous zirconium titanate gels. Work is in hand to evaluate the effectiveness of this chemical process for the preparation of other muticomponent oxides.

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