Nonhydrolytic Sol−Gel Process: Aluminum Titanate Gels

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The efficiency of the nonhydrolytic sol−gel process based on the condensation between metal chlorides and metal alkoxides has been studied in the preparation of aluminum titanate gels. Solutions of aluminum and titanium precursors in the ratio Al/Ti = 2 gave gels with the same metal ratio. The structural evolution of the samples is unusual; they directly crystallize at $T > 600$ °C into metastable pseudo-brookite β-Al_2TiO_5 and are reluctant to decompose into stable TiO_2 (rutile) and α-Al_2O_3 at 1150 °C. This behavior must be connected to the high homogeneity of the samples originating from the nonhydrolytic sol−gel process.

Introduction

Aluminum titanate is considered as a promising refractory material owing to its low thermal expansion coefficient and its high melting point.[1] However this compound is not stable below 1180 °C; it decomposes into TiO_2 (rutile) and α-Al_2O_3 at low temperatures, although metastable Al_2TiO_5 can be preserved at room temperature. It has been prepared by conventional ceramic processing of oxides,[2,3] chemical vapor deposition,[4] and sol−gel processing.[5−12] Formation of Al_2TiO_5 occurs above 1300 °C. The low expansion results from microcracking that occurs during cooling and confers low mechanical strength.[3] To improve the mechanical strength of Al_2TiO_5 materials, work has been done to reduce the formation temperature of the aluminum titanate phase and to reduce the crystalline size, thereby controlling the microcracks.[12] Sol−gel processes have been studied in this connection. However, whatever the precursors used, boehmite, bayerite, or aluminum nitrate and titanium alkoxides, or mixtures of aluminum and titanium alkoxides, the powders or gels obtained undergo phase separation on heating, with crystallization of rutile between 710 and 770 °C, and α-Al_2O_3 between 910 and 1100 °C.[5−12] Formation of Al_2TiO_5 occurs above 1300 °C. Only in one case has direct crystallization of Al_2TiO_5 from the gel been observed at 730 °C, with phase separation into rutile at 930 °C and α-Al_2O_3 at 1230 °C.[10] This result was attributed to the homogeneity of the gel. Indeed, aluminum titanate gel was prepared by hydrolysis of a mixture of aluminum *sec*-butoxide modified with ethyl acetoacetate and titanium isopropoxide modified with acetic acid.[10] Modification of precursors is known to slow the reactivity of alkoxides allowing the formation, for example, of monolithic gels.[13] Futhermore, it has been shown that homogeneous mixtures may crystallize at low temperature into metastable phases if the low rates of diffusion hinder the phase separation into simple oxides; in other words, short-range ordering is preferred to long-range diffusion at low temperatures.[14] Therefore, direct crystallization of metastable aluminum titanate below its temperature range of stability may be considered a criterion for high homogeneity in the precursor gel.

We have developed another route to the preparation of gels which involves nonhydrolytic condensation of metal chlorides with metal alkoxides according to eqs 1a and 1b:[15−22] Formation of alkoxide groups may be performed in situ by reaction of the metal chloride with ether.

$$MCl_n + M(OR)_n \rightarrow 2MO_{n/2} + nRCl \qquad (1a)$$

$$M{-}Cl + ROR \rightarrow M{-}OR + RCl \qquad (1b)$$

Starting with a mixture of two different metals M and M′, the formation of purely alternating M−O−M′ bonds

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[1] Buessem, W. R.; Thielke, N. R.; Sarakauskas, R. V. *Ceram. Age* **1952**, *60*, 38.

[2] Freudenberg, B.; Mocellin, A. *J. Am. Ceram. Soc.* **1987**, *70***,** 33; **1988**, *71*, 22.

[3] Thomas, H. A. J.; Stevens, R. *Brit. Ceram. Trans. J.* **1989**, *88*, 184.

[4] Hori, S.; Kubita, R. *Int. High Technol. Ceram.* **1985**, *1*, 59.

[5] Barringer, E. A.; Bowen, H. K. *J. Am. Ceram. Soc.* **1982**, *65*, C199.

[6] Brugger, P. A.; Mocellin, A. *J. Mater. Sci.* **1986**, *21*, 4435.

[7] Woignier, T.; Lespade, P.; Phalippou, J.; Rogier, R. *J. Non-Cryst. Solids* **1988**, *100*, 325.

[8] Mani, T. V.; Varma, H. K.; Warrier, K. G.; Damodaran, A. D. *J. Am. Ceram. Soc.* **1991**, *74*, 1807.

[9] Prasadarao, A. V.; Selvaraj, U.; Komarneni, S.; Bhalla, A. S.; Roy, R. *J. Am. Ceram. Soc.* **1992**, *75*, 1529.

[10] Bonhomme-Coury, L.; Lequeux, N.; Mussotte, S.; Boch, P. *J. Sol-Gel Sci. Technol.* **1994**, *2*, 371.

[11] Lee, H. L.; Lee, H. S. *J. Mater. Sci. Lett.* **1994**, *13*, 316.

[12] Vasudevan, A. K.; Mani, T. V.; Damodaran, A. D.; Warrier, K. G. K. *J. Mater. Sci. Lett.* **1995**, *14*, 1317.

[13] Doeuff, S.; Henry, M.; Sanchez, C.; Livage, J. *J. Non-Cryst. Solids* **1987**, *89*, 206. Sanchez, C.; Livage, J.; Henry, M.; Babonneau, F. *J. Non-Cryst. Solids* **1988**, *100*, 65. Doeuff, S.; Henry, M.; Sanchez, C. *Mater. Res. Bull.* **1990**, *25*, 1519.

[14] Barboux, P.; Griesmar, P.; Ribot, F.; Mazerolles, L. *J. Solid State Chem.* **1995**, *117*, 343.

[15] Corriu, R. J. P.; Leclercq, D.; Lefèvre, P.; Mutin, P. H.; Vioux, A. *J. Non-Cryst. Solids* **1992**, *146*, 301; *J. Mater. Chem.* **1992**, *2*, 673; *Chem. Mater.* **1992**, *4*, 961.

[16] Acosta, S.; Corriu, R. J. P.; Leclercq, D.; Lefèvre, P.; Mutin, P. H.; Vioux, A. *J. Non-Cryst. Solids* **1994**, *170*, 234.

[17] Arnal, P.; Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Vioux, A. *Mater. Res. Soc. Symp. Proc.* **1994**, *346*, 339.

[18] Acosta, S.; Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Vioux, A. *J. Sol-Gel Sci. Technol.* **1994**, *2*, 25.

[19] Acosta, S.; Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Vioux, A. *Mater. Res. Soc. Symp. Proc.* **1994**, *346*, 345.

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would be expected; however, ligand exchange between chloride and alkoxide ligands also takes place (eq 2).[16−25]

$$\mathrm{M{-}Cl + M'{-}OR \rightleftharpoons M{-}OR + M'Cl} \qquad (2)$$

Homogeneous bicomponent gels with a high level of M−O−M′ bonds may be obtained if the rate of heterocondensation is higher (or of the same order) as that of homocondensation. We have already shown that silica−alumina gels prepared in this way are homogeneous at the atomic level, as evidenced by ^{29}Si NMR and X-ray spectroscopies.[18−20] The homogeneity of nonhydrolytic zirconium titanate gels has been established, based on their direct crystallization into $TiZrO_4$ at $T \approx 700$ °C.[22]

In this paper, we describe the preparation and the thermal behavior of aluminum titanate gels prepared by the nonhydrolytic sol−gel process.

Experimental Section

Starting Materials. Titanium tetrachloride (Jansen), titanium isopropoxide (Jansen), aluminum isopropoxide, and aluminum trichloride (Aldrich) were used as received; diisopropyl ether was distilled from sodium/benzophenone before use; dichloromethane and chloroform were distilled from P_2O_5. α-Alumina (Aldrich, 99.9%) and TiO_2 (rutile) (Aldrich, 99.9%) were heat-treated separately for 5 h at 1200 °C.

Preparation of Samples. The preparation of samples was carried out under argon in oven-dried glassware.

Gel 1: In a glovebag under argon, 4.87 g (0.36 mol) of $AlCl_3$ was put into a Schlenk tube. Then the tube was removed, attached to a Schlenk line, and cooled to 0 °C. By syringe, 1.76 g (0.008 mol) of $Al(O^iPr)_3$ dissolved in 13.8 mL of CH_2Cl_2 and 5.94 g (0.021 mol) of $Ti(O^iPr)_4$ was successively added with stirring to aluminum chloride. After addition, the homogeneous light green solution was warmed to room temperature and transferred to another tube by means of a cannula. The tube was frozen in liquid nitrogen and then sealed under vacuum. The sealed tube was held at 110 °C in an oven. After 10 h a green gel, soaking in a colorless syneresis liquid, was formed. After 7 days at 110 °C, the tube was opened in a glovebag under argon. The solid and the liquid phases were separated by filtering. The isolated gel was washed successively with fractions of dichloromethane and dried under vacuum at room temperature. The cracked sample was ground in a glovebox under argon and dried under vacuum at 110 °C for 3 h, affording 8.35 g of xerogel.

Gel 2: The above procedure was used. In a Schlenk tube, 5.78 g (0.043 mol) of $AlCl_3$ was suspended in 13.5 mL of CH_2Cl_2. To the stirred suspension were added at 0 °C, by means of syringes, 2.4 mL (0.022 mol) of $TiCl_4$ and 14.5 mL (0.103 mol) of diisopropyl ether. The homogeneous brown solution was then stirred at room temperature and transferred to a tube which was sealed. After 3 h at 110 °C, a pink gel was formed which turned brown after 7 days at 110 °C. The solid and the liquid were separated and treated as above; 8.62 g of xerogel was obtained.

Gel 3: To 1 g (0.0075 mol) of $AlCl_3$, in a Schlenk tube, were added, at 0 °C, 7.67 g (0.037 mol) of $Al(O^iPr)_3$ dissolved in 13.2 mL of CH_2Cl_2 and then 2.4 mL (0.0217 mol) of $TiCl_4$. After warming to room temperature, the homogeneous brown solution was treated as above. After 10 h at 110 °C, a clear brown gel was obtained. After 7 days at 110 °C, 8.1 g of gel was isolated by the above procedure.

Gel 4: To 2.92 g (0.0219 mol) of $AlCl_3$, in a Schlenk tube, were successively added, at 0 °C with stirring, 4.44 g (0.0217 mol) of $Al(O^iPr)_3$ dissolved in 12.9 mL of CH_2Cl_2, 1.2 mL (0.0108 mol) of $TiCl_4$, and 3.4 mL (0.011 mol) of $Ti(O^iPr)_4$. The brown solution was warmed to room temperature and transferred to a tube which was sealed. After 10 h at 110 °C a brown gel was obtained which was left at 110 °C for 7 days; 6.09 g of gel was then isolated by the above procedure.

The syneresis liquids were analyzed by ^{1}H and ^{13}C NMR and GC. The ^{1}H NMR spectrum showed a doublet at $\delta = 1.5$ ppm, 6H, and a septuplet at $\delta = 4.2$ ppm; the ^{13}C spectrum showed signals with chemical shifts at $\delta = 27.5$ ppm ($(CH_3)_2CHCl$) and $\delta = 54.1$ ppm (CH_2Cl_2 and $(CH_3)_2CHCl$). Comparison with authentic samples showed that they were due to CH_2Cl_2 (solvent of the reaction) and ^{i}PrCl.

Characterization Techniques. Thermogravimetric and differential thermal analyses were performed in a 20/80 mixture of oxygen and nitrogen, on a thermobalance Netzsch STA 409 using a 10 K/ min heating rate.

The thermogravimetric analyzer was coupled to a Balzers QMG 421 quadrupole mass spectrometer (ionization energy 70 eV). The volatile products were sampled above the crucible by a stainless steel capillary (internal diameter 0.25 mm) connected to the mass spectrometer. A scan from 2 to 150 amu was collected and stored every 30 s. It is possible either to plot mass spectra obtained at selected temperatures or to plot the evolution of the signal of characteristic ions as a function of temperature.

X-ray powder diffraction patterns were recorded with Cu Kα radiation using a Siefert MZ IV diffractometer (five scans, with 1000 digitized points and 500 ms acquisition time, θ angle ranging from 5 to 40°). Phase identification was performed by comparison with the JCPDS data cards: Al_2TiO_5 (JCPDS file 26-40), α-Al_2O_3 (JCPDS file 10-173), and rutile (JCPDS file 21-1276). Phase separation of β-Al_2TiO_5 into TiO_2 (rutile) and α-Al_2O_3, for different annealing time at 1150 °C, was estimated from the specific surfaces of the reflection (110) of β-Al_2TiO_5, (113) of α-alumina, and (110) of TiO_2 (rutile). The equation of phase separation is

$$\mathrm{Al_2TiO_5 \rightarrow Al_2O_3 + TiO_2}$$

$$\mathrm{A \rightarrow B + C}$$

Then $n_B = n_C$ and $n_A + n_B = n_A + n_C = 100$, where n_A, n_B, and n_C are the mole fractions of Al_2TiO_5, Al_2O_3, and TiO_2, respectively. The general relationship between XRD intensity and concentration of the phases present gives $n_B/n_A = K_1I_B/I_A$ and $n_C/n_A = K_2I_C/I_A$ and $n_A = [100/(1 + K_1I_B/I_A)] = [100/(1 + K_2I_C/I_A)]$; I_i are the integral intensity of the selected diffraction lines and K_1 and K_2 are constant. K_1 was determined by making up a mixture of 0.1 g (0.55 mmol) of β-Al_2TiO_5 (prepared by annealing gel 1 for 5 h at 1500 °C) and 0.1 g (0.98 mmol) of α-Al_2O_3. XRD of the mixture gave a ratio $I_B/I_A = 1.31$, which implies $K_1 = 2.37$. K_2 was obtained by the same procedure starting from a mixture of 0.3 g (1.65 mmol) of β-Al_2TiO_5 and 0.3 g (3.76 mmol) of TiO_2 (rutile) which gave a ratio $I_C/I_A = 0.76$ corresponding to $K_2 = 0.74$. The amount of amorphous phase in the gel 2 annealed 5 h at 850 °C was determined from a mixture of 0.194 g (1.07 mmol) of gel 2 and 0.269 g (2.47 mmol) of α-Al_2O_3 ($n_B/n_A = 2.31$) The surfaces of the caracteristic peaks gave a ratio $I_B/I_A = 1.16$ which corresponds to $n_B/n_A = 2.04$. The amount of amorphous phase was about 10%.

NMR spectroscopy was performed with a Bruker AW 80 instrument (^{1}H NMR spectra) using the solvent CH_2Cl_2 as lock and as internal reference and with a Bruker AC 250 (^{13}C NMR spectra) operating at 62.9 MHz, with $CDCl_3$ as a solvent and internal standard, power-gated decoupling sequence with repetition time of 2 s at 90° being used.

Gas chromatography was performed on a Girdel Série 3000 apparatus equipped with a DB-5 capillary column of 30 m. Dinitrogen was used as vector gas (0.3 bar). The temperatures used were 45 °C for the oven, 80 °C for the injector, and 150

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(20) Acosta, S.; Arnal, P.; Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Vioux, A. *Mater. Res. Soc. Symp. Proc.* **1994**, *346*, 43.

(21) Vioux, A.; Leclercq, D. *Heterog. Chem. Rev.* **1996**, *3*, 65.

(22) Andriamananarivelo, M.; Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Vioux, A. *J. Mater. Chem.* **1997**, *7*, 279.

(23) Bradley, D. C.; Hill, D. A. W. *J. Chem. Soc.* **1952**, 2773.

(24) Weingarten, H.; Van Wazer, J. R. *J. Am. Chem. Soc.* **1965**, *87*, 724.

(25) Moedritzer, K. In *Organometallic Reactions*; Becker, E. I., Tsutsui, M., Eds.; Wiley-Interscience: New York, 1971; Vol. 2, pp 1−116.

Table 1. Chemical Analyses and Condensation Degree of the Dried Gels (3 h, 110 °C in Vacuum)

	elemental analyses (%)					
gel	C	Cl	Al	Ti	composition of dried gels	cd[a] (%)
1	14.87	14.85	11.85	8.85	$AlTi_{0.42}Cl_{0.95}(O^iPr)_{0.94}O_{1.40}$	60
2	17.82	12.59	9.80	8.45	$AlTi_{0.49}Cl_{0.98}(O^iPr)_{1.36}O_{1.31}$	53
3	20.42	23.11	12.50	10.70	$AlTi_{0.48}Cl_{1.41}(O^iPr)_{1.22}O_{1.15}$	47
4	20.92	22.91	12.55	12.00	$AlTi_{0.54}Cl_{1.39}(O^iPr)_{1.25}O_{1.26}$	49

[a] Condensation degree.

°C for the detector (flame ionization). The retention time of 156 s corresponds to that of authentic ^{i}PrCl.

Elemental analyses were performed by the "Service Central d'Analyses du CNRS France". Aluminum and titanium contents were determined by induction coupled plasma (ICP) from an aqueous solution. Carbon and hydrogen contents were established by high-temperature combustion and IR spectroscopy. Chlorine content was measured by potentiometric titration. The oxygen content was determined by difference.

On calcined samples, the Al and Ti contents were also determined on powder coated by carbon, using an energy-dispersive X-ray analyzer (Link AN 1000), fitted to a SEM Cambridge Stereoscan 360 (25 kV acceleration potential, 33.0° takeoff angle, 7.5 mm thick Be window), using cobalt as a standard.

Results and Discussion

Preparation and Characterization of Gels. Four aluminum titanate gels with an Al-to-Ti ratio of 2 were prepared from different solutions of precursors (see Experimental Section). In all cases, an equal number of chloride and alkoxide functions (added as alkoxide or formed in situ by reaction with ether) was used. Whatever the starting solution, gelation occurs at 110 °C in sealed tubes in less than 10 h. The formation of isopropyl chloride, identified by gas chromatography and ^{1}H and ^{13}C NMR spectroscopy, proved the nonhydrolytic nature of the condensations.

The composition of the dried gels was determined by elemental analysis of the dried samples. Assuming that, after 3 h at 110 °C under vacuum, no isopropyl chloride and solvent remained in the xerogel, carbon was considered to come from residual alkoxide groups and chlorine from chloride functions. The bridging oxygen content was then calculated, knowing the alkoxide and chloride content, by taking into account the valence of the metal atoms (Table 1). The condensation degree of the xerogels was deduced as a ratio of bridging oxygen to the expected one in the oxide of the same composition. For example, for a composition of xerogel $AlTi_xCl_y(OR)_zO_m$, $m = [3 + 4x) - (y + z)]/2$ and the condensation degree (%) is $[m/(1.5 + 2x)]100$. The condensation degree of the gels does not dramatically change with the precursors and is rather low, around 50%.

Calcination. The thermogravimetric analysis (TGA) curves of the four gels are similar. An example is given in Figure 1. Two mass loss events are observed. These events were monitored by a mass spectrometer coupled with a TGA apparatus (Figure 2). The first step (from 100 to 300 °C) corresponds to the loss of propene (*m/z* 41) and HCl (*m/z* 36) and the second one (from 300 to 600 °C) to the loss of CO_2 (*m/z* 44) and HCl. No isopropyl chloride (*m/z* 63) was detected, indicating that any nonhydrolytic condensation does not take place during calcination. Formation of propene may be due to the thermal degradation of alkoxide groups which would occur with formation of propene and hydroxyl groups (eq 3).[25]

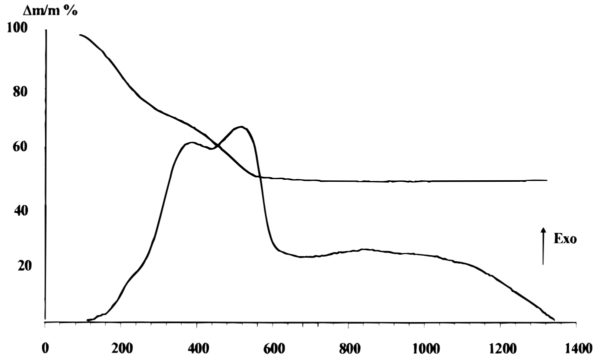


Figure 1. TGA DTA curves of aluminum titanate gel.

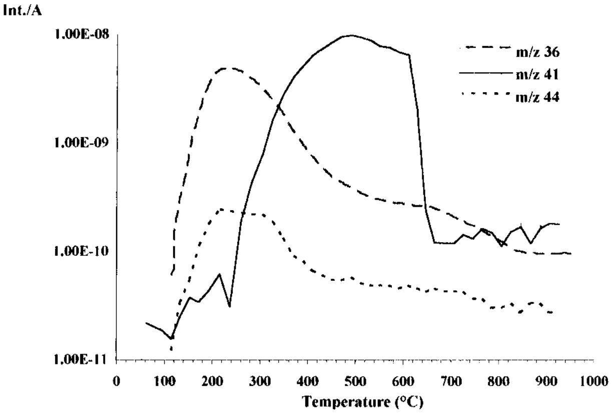
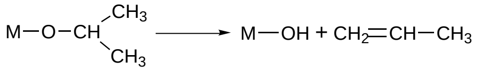


Figure 2. Analyses of the gases evolved during calcination of gel 2.

Table 2. Thermal Analyses of Aluminum Titanate Gels

	Δ*m*/*m*		
gel	calcd (%)	found (TGA)%	yield (%)
1	48	49	100
2	52	47	100
3	53	51	97
4	52	52	73



$$M{-}O{-}CH(CH_3)_2 \longrightarrow M{-}OH + CH_2{=}CH{-}CH_3 \qquad (3)$$

The escape of HCl at this stage may be explained by the condensation between hydroxyl and chloride groups (eq 4).

$$M{-}OH + M{-}Cl \rightarrow M{-}O{-}M + HCl$$

In the second step, oxidation of organic residue with formation of CO_2 and radical cleavage of chlorine with formation of HCl take place.

Weight losses during calcination of xerogels are large, from 47 to 52%, and are related to their low degrees of condensation (Table 2). Note that weight losses of the same order are observed for gels prepared by the hydrolytic sol−gel process.[6,7,9,10]

The weight losses resulting from the formation of oxide may be calculated from the composition of the xerogels according to

$$AlTi_xCl_y(OR)_zO_m \rightarrow AlTi_xO_{1.5+2x} + \text{gas}$$

Table 3. Al/Ti Ratio and Cl Content of Aluminum Titanate Gels (Determined by Elemental Analyses)

	Al/Ti		Al/Ti 600 °C			Al/Ti 850 °C		
run	nominal	150 °C (ICP)	ICP	EDX	Cl wt % 600 °C (ICP)	ICP	EDX	Cl wt % 850 °C (ICP)
1	2.1	2.4	2.3	2.4	<0.2	2.4	1.9	
2	2.0	2.0	2.2	2.1	0.81	2.1	2.0	<0.2
3	2.1	2.1	2.0	2.0	0.88	2.3	1.9	<0.2
4	2.0	1.9	2.0	1.9	<300 ppm	2.0	1.9	<300 ppm

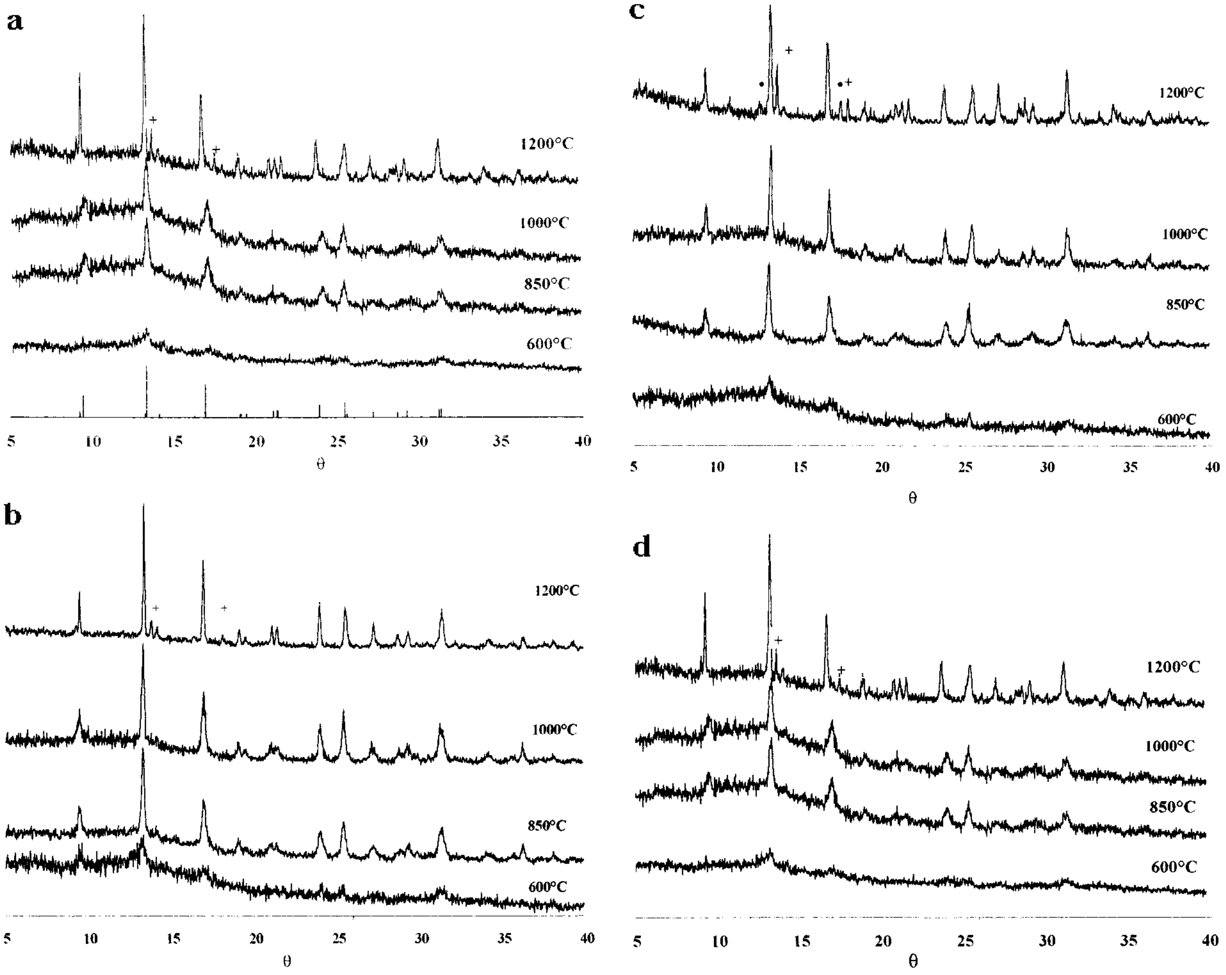


Figure 3. X-ray diffraction of samples calcined at 600, 850, 1000, and 1200 °C: (a) gel 1, (b) gel 2, (c) gel 3, (d) gel 4, + TiO_2-(rutile), (●) α-Al_2O_3.

The good agreement between the calculated weight losses and the experimental ones determined by TGA (Table 2) shows that the determinations of the xerogel compositions (Table 1) are reliable.

The yields in oxide, after calcination, are reported in Table 2; they are rather good, indicating that, by this process, the two metals introduced in solution as alkoxides or chlorides were incorporated in the gel, as confirmed by analysis. Indeed, Table 3 shows the Al-to-Ti ratio determined by analyses (EDX and/or ICP) in xerogels and samples heat-treated at 600 and 850 °C. These ratios are close to the starting solution composition (stoichiometric aluminum titanate). Furthermore, the EDX analysis of randomly selected particules of each sample, using a spot size of 1 μm, indicated Al-to-Ti ratios around 2. This means that the samples are homogeneous on the nanoscale, with a Al/Ti ratio of ≈2. The residual Cl content at 600 °C ranges from 0.88 wt % (atomic ratio $Cl/Al_2TiO_5 = 0.05$) to less than 0.2 wt %, which is the threshold of detection in current analysis by ICP. The Cl content, after calcination at 850 °C, is less than 0.2 wt %. Trace analysis on gel 4 indicates a Cl content below the threshold of detection (300 ppm) at 600 and 850 °C. In any case, after calcination at 850 °C, the residual chlorine content of the gels is under the threshold of detection.

Crystallization. As shown in Figure 1, the DTA curves of the xerogels do not show any exothermic peaks above 600 °C. This contrasts with the behaviors reported for hydrolytic gels, where two exotherms corresponding to rutile and α-alumina crystallization and an endotherm due to β-Al_2TiO_5 crystallization are observed.[5−12] XRDs of samples heated at 600, 850, 1000, and 1200 °C (5 h holding time at each temperature) are displayed in Figure 3. The samples are almost amorphous at 600 °C. At 850 °C, only crystallization of pseudo brookite β-Al_2TiO_5 occurs, without formation of TiO_2 or Al_2O_3. About 10% of amorphous phase is present at this temperature. At 1000 °C, only lines for β-Al_2TiO_5 are present. At 1200 °C only small amounts of rutile and α-alumina may be detected besides β-Al_2TiO_5.

This structural evolution with temperature is very unexpected. The direct crystallization of β-Al_2TiO_5 at

Table 4. % Al_2TiO_5 in Function of Annealing Time at 1150 °C

annealing time (h)	% Al_2TiO_5			
	gel 1	gel 2	gel 3	gel 4
0	89	93	92	98
25	23	87		
48	19	83	44	71
73	11			
96		42	43	23
144		21	6	

$T > 600$ °C, as in the case of the gel obtained by hydrolysis of modified precursors, shows that the gels prepared by nonhydrolytic condensations are homogeneous. However, in the work of Bonhomme-Coury et al., the gel segregated into thermodynamically stable rutile and corundum at higher temperature.[10,14] On the other hand, β-Al_2TiO_5 prepared by the nonhydrolytic route did not phase separate below its stability domain, which is over 1180 °C. At 1200 °C, only small amounts of rutile and corundum could be detected.

Stoichiometric Al_2TiO_5, prepared by calcination of a powder mixture of Al_2O_3 and TiO_2 above 1300 °C, was shown to totally phase separate to TiO_2 and Al_2O_3, within 5−50 h, depending on average grain size, at 1150 °C, which is the temperature at which the most rapid segregation occurred.[28,29] We have qualitatively followed the phase separation of the nonhydrolytic aluminum titanate samples at this temperature as a function of annealing time, by comparing the specific intensities of the reflection (110) of Al_2TiO_5, (113) of α-alumina, and (110) of TiO_2 (rutile). Table 4 and Figure 4 show that phase separation into TiO_2 and Al_2O_3 requires more than 70 h of heating at 1150 °C. The rate of decomposition depends on the starting gel. The half-time of decomposition increases in the order gel 1, gel 3, gel 4, gel 2.

Stabilization of aluminum titanate is known to be obtained by addition of more than 2 wt % of lanthanides, Fe_2O_3, MgO, SiO_2, SnO_2, CaO, etc.[27] However, in our samples, EDAX analyses did not show any metals other than Al and Ti. Futhermore, the residual Cl content in the samples calcined at 850 °C is below the threshold of detection of ICP analysis (300 ppm). Thus, the origin of the stabilization of the metastable phase β-Al_2TiO_5 cannot be attributed to the presence of such elements.

Formation of metastable phases below their domain of stability has already been reported.[10,30−32] The crystallization into a metastable phase results from the homogeneity of the amorphous phase which favors short-range ordering when long-range diffusion is inhibited.[14,27] However, when diffusion is possible, phase separation occurs. In the case of aluminum titanate prepared from a mixture of Al_2O_3 and TiO_2 at 1500 °C, it has been shown that phase separation occurs by a mechanism of nucleation and growth.[29] In such a mechanism, the size of the grain particules is determinant and phase separation may be inhibited when the size remains below the critical size for nucleation.[31] Phase separation of Al_2TiO_5 into Al_2O_3 and TiO_2 appears below 1000 °C in the case of Bonhomme-Coury et al., while it is not complete after 70 h at 1150 °C for aluminum titanate obtained by the nonhydrolytic route. Although the critical size of phase separation is unknown in the case of Al_2TiO_5, the high stability of aluminum titanate prepared by the nonhydrolytic route may be ascribed to the formation of small crystallites, embedded in the amorphous phase (10% at 850 °C), which would be reluctant to grow beyond the critical size.

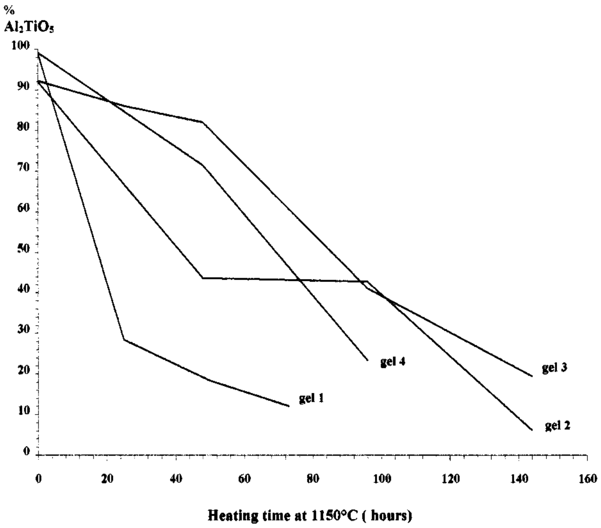


Figure 4. Decomposition rate of Al_2TiO_5 samples at 1150 °C.

Conclusion

The nonhydrolytic sol−gel process based on the condensation between metal chlorides and metal alkoxides leads to the formation of aluminum titanate gels in high yields.

The Al-to-Ti ratios are constant throughout the process, from the solution of precursors to the final oxide.

The direct crystallization of metastable β-Al_2TiO_5 at 850 °C shows that highly homogeneous aluminum titanate gels can be obtained by the nonhydrolytic sol−gel process. This metastable phase presents an unexpected stability, the origin of which remains to be determined.

The homogeneity obtained, despite the redistribution reactions, shows that a leveling of the condensation rates around the metal atoms has been achieved. The nonhydrolytic sol−gel process, because it leads to very homogeneous gels, is very suited to the preparation of metastable compounds.

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(26) Nandi, M.; Rhubright, D. *Inorg. Chem.* **1990**, *29*, 3065.

(27) Lange, F. F.; Balmer, M. L.; Levi, C. G. *Sol−Gel Sci. Technol.* **1994**, *2*, 317.

(28) Parker, F. J. *J. Am. Ceram. Soc.* **1990**, *73*, 929.

(29) Buscagaglia, V.; Battilana, G.; Leoni, M. *J. Mater. Sci.* **1996**, *31*, 5009 and references therein.

(30) Novet, T.; Johnson, D. C. *J. Am. Chem. Soc.* **1991**, *113*, 3398.

(31) Fister, L.; Johnson, D. C. *J. Am. Chem. Soc.* **1992**, *114*, 4639.

(32) Fister L.; Johnson, D. C.; Brown, R. *J. Am. Chem. Soc.* **1994**, *116*, 629.