

Hydrolysis of Mixed Titanium and Zirconium Alkoxides by an Esterification Reaction

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Received June 11, 1991; in revised form October 21, 1991

Hydrolysis of mixed $\text{Ti}(\text{O}^i\text{Pr})_4$ and $\text{Zr}(\text{O}^n\text{Pr})_4$ in *n*-PrOH has conducted to crystals, gels, or precipitates, depending on the quantity of acetic acid added for the esterification reaction. A structural model of $\text{Zr}_6\text{Ti}_3(\text{OPr})_{16}(\text{OAc})_8\text{O}_6$ clusters is proposed and shows various coordination numbers for the metallic atoms (6, 7, and 8 for Zr and 6 for Ti) and acetate or propyl bridges linking these atoms. A comparative study by IR and ^{13}C NMR spectroscopies shows the molecular structure similarity of crystallized clusters and polymeric species in the gel. Molecular clusters may be considered as intermediate species during gelation. A thermal study of crystals and gel decomposition has been performed. © 1992 Academic Press, Inc.

Introduction

The attractive properties of titanium and zirconium oxides coupled with their interest in the sol-gel process to obtain fibers, thin layers, or submicronic monodispersed powders (1-5) have produced much research on titanium and zirconium alkoxides. These alkoxides are very sensitive to hydrolysis and this reaction can be usually performed by esterification reaction which is able to modify the alkoxide molecules and their reactivity (6, 7). A precise control of the reaction parameters can lead to a stable sol, crystals, a gel, or a precipitate. An accurate characterization of the chemical species formed all along the process and particularly the structural determination of crystals produced a better understanding of the hydrolysis mechanism.

With this background, it seemed very interesting to study the behavior of a mixture of titanium and zirconium alkoxides during hydrolysis. As each single alkoxide leads to a $-M-O-M-$ network (with $M = \text{Ti}$ or Zr), one can hope that a mixture of titanium and zirconium alkoxides will lead to a $-\text{Ti}-O-\text{Zr}-$ network. The purpose of this work is to study this mixed alkoxide system under hydrolysis conditions and to characterize the resulting products. The structural determination of crystals is followed by a comparative study of the structural arrangement in gel and crystals.

Experimental

Product Preparation

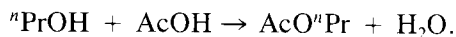
The alkoxides $\text{Ti}(\text{O}^i\text{Pr})_4$ and $\text{Zr}(\text{O}^n\text{Pr})_4$ in *n*-propanol solutions were always taken in a Ti/Zr ratio equal to 1. The concentration of each alkoxide is 0.8 mole l^{-1} versus propa-

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TABLE I
VARIATION OF t_g (gelation time) AND t_c (crystallization time = apparition of the first crystals) WITH TEMPERATURE

h	1	2	3	4	5
Products obtained at 7°C	←————→ stable sol		←————→ crystals		
Delay (days)	>500	>500	200–220	3	2
Products obtained at 20°C	←————→ stable sol		←————→ crystals		
Delay (days)	>500	>500	200–220	3	2
Products obtained at 40°C	←————→ stable sol		←————→ crystals		transparent gel
Delay (days)	>500	>500	200–220	3	90–110

nol. The hydrolysis has been performed by an esterification reaction by adding acetic acid according to the following reaction:



The theoretical hydrolysis ratio h has been defined as the number of acetic acid molecules over the number of alkoxide molecules; the h value varies from 1 to 8 for each alkoxide.

The solutions were maintained with a magnetic stirring during 1 hr at room temperature and then kept at various temperatures from 7 to 40°C. Depending on these parameters, the system can form stable sols, crystals, gels, or precipitates.

Product Characterization

The products resulting from the mixed system have been mainly characterized by thermal analysis (TGA Setaram, DTA Perkin-Elmer), FTIR spectroscopy (Nicolet ZDX), by ^{13}C Nuclear Magnetic Resonance (Bruker AM 300 MHz for solid samples) and X-ray diffraction (Siemens diffractometer for single crystal and multichannel analyzer Inel CPS 120 for powder).

All the characterizations were performed using crystals washed in propanol and gels dried at 100°C.

Results

By varying h and T parameters, different products can be obtained, as shown in Table I. Compared to single alkoxide systems (7), temperature does not act on the behavior of the resulting mixed compounds, except for $h = 5$. In this last case, we observe a crystallization at 7 and 20°C and a gelation at 40°C. For $h > 5$, a precipitate is always obtained. The crystals obtained in this study have the same crystallographic parameters. When the crystallization occurs, there is no gelation and a very stable solution above the crystals is observed.

Gels are transparent in the case of zirco-

TABLE II
CRYSTALLOGRAPHIC DATA FOR
 $\text{Zr}_6\text{Ti}_3(\text{OPr})_{16}(\text{OAc})_8\text{O}_6$

	Formula molecular weight	$\text{Zr}_6\text{Ti}_3\text{C}_{64}\text{H}_{136}\text{O}_{38}$	
		2203.54 g	
Space group	$P\bar{1}$	Z	2
a	14.692(2) Å	d meas.	1.45
b	16.359(3) Å	d calc.	1.48
c	22.986(4) Å	λ MoK α	0.71069 Å
α	82.53(1)°	μ	0.904 mm $^{-1}$
β	81.85(1)°	R	0.12
γ	65.45(1)°		
v	4959(1) Å 3		

TABLE III
 ATOMIC POSITION PARAMETERS AND THERMAL AGITATION FACTORS U_{eq} OF METALLIC ATOMS
 AND OXYGEN ($\times 10^3$)

Atoms	<i>x</i>	<i>y</i>	<i>z</i>	$U(\text{\AA}^2)$	Atoms	<i>x</i>	<i>y</i>	<i>z</i>	$U(\text{\AA}^2)$
Zr ₁	4(1)	246(1)	240(1)	54(4)	O ₂₅	-86(1)	252(2)	335(1)	39(17)
Zr ₂	200(1)	253(1)	142(1)	65(3)	O ₂₆	-19(3)	195(3)	34(1)	260(42)
Zr ₃	168(1)	165(1)	347(1)	90(3)	O ₂₇	146(2)	227(1)	70(1)	80(20)
Zr ₄	225(1)	50(1)	228(1)	101(4)	O ₂₈	187(3)	482(2)	124(1)	297(40)
Zr ₅	141(1)	369(1)	261(1)	210(6)	O ₂₉	36(2)	486(2)	241(1)	220(31)
Zr ₆	48(1)	169(1)	103(1)	262(9)	O ₃₀	448(2)	-174(2)	346(1)	413(36)
Ti ₇	944(1)	330(1)	377(1)	154(8)	O ₃₁	251(2)	247(2)	312(1)	206(32)
Ti ₈	389(1)	946(1)	327(1)	76(7)	O ₃₂	-161(3)	431(2)	327(1)	357(47)
Ti ₉	320(1)	403(1)	171(1)	221(12)	O ₃₃	384(2)	-22(2)	403(3)	63(25)
O ₁₀	87(1)	314(1)	202(1)	76(18)	O ₃₄	-69(3)	169(5)	236(1)	114(34)
O ₁₁	108(1)	140(1)	282(1)	38(16)	O ₃₅	272(2)	-13(1)	136(1)	189(31)
O ₁₂	124(2)	159(1)	172(1)	83(20)	O ₃₆	385(2)	369(2)	101(1)	150(25)
O ₁₃	336(2)	248(2)	73(1)	70(21)	O ₃₇	128(2)	376(2)	241(1)	110(25)
O ₁₄	54(2)	297(1)	314(1)	131(23)	O ₃₈	275(2)	124(2)	419(1)	150(26)
O ₁₅	300(2)	132(2)	180(1)	56(20)	O ₃₉	361(2)	-76(2)	252(2)	71(21)
O ₁₆	256(2)	311(2)	188(1)	134(30)	O ₄₀	122(5)	420(2)	347(1)	598(85)
O ₁₇	141(2)	384(1)	92(1)	78(20)	O ₄₁	-26(5)	426(4)	399(2)	369(96)
O ₁₈	287(2)	64(1)	303(1)	71(18)	O ₄₂	162(3)	39(2)	80(1)	343(46)
O ₁₉	57(2)	227(2)	417(1)	146(27)	O ₄₃	492(3)	-40(3)	302(2)	221(49)
O ₂₀	141(2)	48(1)	397(1)	94(21)	O ₄₄	-33(5)	99(2)	151(1)	292(48)
O ₂₁	264(2)	-78(1)	372(1)	133(28)	O ₄₅	236(3)	443(2)	251(2)	184(15)
O ₂₂	-46(2)	275(2)	146(1)	100(21)	O ₄₆	452(3)	328(3)	189(2)	308(54)
O ₂₃	154(3)	26(2)	239(1)	254(41)	O ₄₇	372(4)	499(5)	138(3)	275(61)
O ₂₄	-152(3)	339(2)	438(1)	339(55)					

Note. Standard deviations are in brackets.

nium *n*-propoxide and opaque for titanium isopropoxide. In the mixed system, gels are always transparent. The corresponding crystals are transparent, colorless plates.

X-ray Structure Data

Elementary analysis of crystals leads to the following formula: Zr₆Ti₃C₆₄H₁₃₆O₃₈ (molecular weight = 2203.54 g). This crystal was obtained using the following preparation parameters: $h = 4$ and $T = 20^\circ\text{C}$.

The crystalline structure has been determined by single crystal X-ray diffraction. Dimension of the crystal are $0.30 \times 0.20 \times 0.05$ mm. Analysis of Weissenberg photographs yielded a triclinic unit cell. The space group is $P\bar{1}$. The corresponding crystallo-

graphic data are given in Table II. The structure was solved by direct methods and all refinements were performed by using Shelx 76 programs (8). Of 9131 reflections that have been recorded, only 4864 have been used for the structure determination with $F > 5\sigma(F)$. Intensities were only corrected for Lorentz and polarization factors. Scattering factors were those of the "International Tables of X-ray Crystallography" (9).

During the refinements, it has been impossible to differentiate *i*-PrO and *n*-PrO groups because of their strong thermal agitation; the propoxy chains show a considerable disorder. Fractional site occupancy was unfruitfully tested during the refinements; a collection at lower temperature is necessary

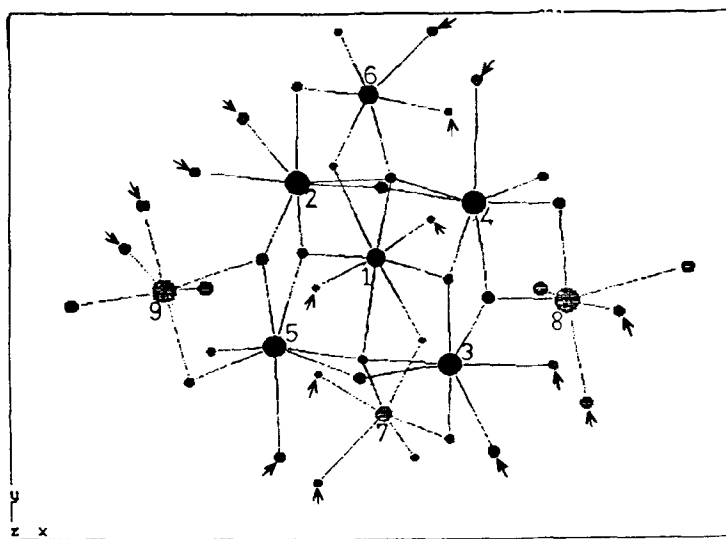


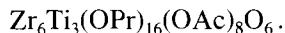
FIG. 1. Structural model of $Zr_6Ti_3(OPr)_{16}(OAc)_8O_6$: (●: 1 → 6: Zr; ○: 7 → 9: Ti; →●: oxygen atoms of acetate groups; ●: oxygen atoms of propyl groups or μ -oxygen).

to determine the precise position of carbon atoms of the propyl groups. So, in the structure description, OPr and propoxy groups can mean either *n*-PrO or *i*-PrO.

As the most important aspect was the determination of the metal atom environments, the last refinement was performed with the following temperature factors: anisotropic for Zr, Ti, and O atoms, and isotropic for C atoms of acetate groups. The C atoms of propyl chains were not refined and their atomic coordinates were those of the Fourier difference. With these conditions, the coefficient *R* was 0.12.

Atomic coordinates of metal and oxygen atoms are reported in Table III.

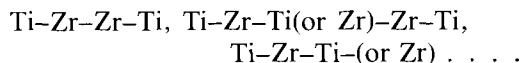
Figure 1 shows the structural model; it is formed by a cluster of 9 metallic atoms: 6 zirconium and 3 titanium atoms. There are one 8-, four 7-, and one 6-coordinate zirconium atoms in the structure and three 6-coordinate titanium atoms. There are 8 acetate groups, 16 propoxy chains, and 6 oxygen atoms bond to the metal atoms (2 μ_4 -oxo and 4 μ_3 -oxo). The developed formula can be written as



Two types of ligands can be observed: bridging (8 acetate and 8 propoxy groups) and terminal (8 propoxy groups).

In Table IV, interatomic distances are reported. In the square antiprism (coordination number 8), the Zr–O distances vary from 1.99 to 2.38 Å; in the monocapped trigonal prism (coordination number 7), the Zr–O bonds take values from 1.90 to 2.36 Å; in the octahedral environment (coordination number 6), the Zr–O bond length varies from 1.90 to 2.18 Å and Ti–O bonds from 1.80 to 2.15 Å.

The environments of metal atoms are not equivalent and are reported in Table V. The oxygen bridges allow the formation of chains of metal atoms like



Infrared Spectroscopy

Crystal. The IR spectrum of crystals dispersed in KBr, after washing in propanol, is

TABLE IV
DISTANCES OF M-O BONDS IN THE STRUCTURE
Zr₆Ti₃(OPr)₁₆(OAc)₈O₆

Metallic atoms environment					
Zr ₁ -O ₁₀	2.00(2)	Zr ₂ -O ₁₀	2.01(2)	Zr ₃ -O ₁₁	2.01(2)
Zr ₁ -O ₁₁	2.01(2)	Zr ₂ -O ₁₂	2.24(2)	Zr ₃ -O ₁₄	2.24(2)
Zr ₁ -O ₁₂	2.30(2)	Zr ₂ -O ₁₃	2.35(2)	Zr ₃ -O ₁₈	2.09(2)
Zr ₁ -O ₁₄	2.30(2)	Zr ₂ -O ₁₅	2.09(2)	Zr ₃ -O ₁₉	2.14(2)
Zr ₁ -O ₂₂	2.32(2)	Zr ₂ -O ₁₆	1.95(2)	Zr ₃ -O ₂₀	2.25(2)
Zr ₁ -O ₂₅	2.38(2)	Zr ₂ -O ₁₇	2.18(2)	Zr ₃ -O ₃₁	2.18(2)
Zr ₁ -O ₃₄	1.99(2)	Zr ₂ -O ₂₇	2.09(2)	Zr ₃ -O ₃₈	2.29(2)
Zr ₁ -O ₃₇	2.21(2)				
Zr ₄ -O ₁₁	2.11(2)	Zr ₅ -O ₁₀	2.12(2)	Zr ₆ -O ₁₂	2.02(2)
Zr ₄ -O ₁₂	2.19(3)	Zr ₅ -O ₁₄	2.21(2)	Zr ₆ -O ₂₂	1.99(2)
Zr ₄ -O ₁₅	2.19(2)	Zr ₅ -O ₁₆	2.21(3)	Zr ₆ -O ₂₆	1.90(2)
Zr ₄ -O ₁₈	2.14(2)	Zr ₅ -O ₂₉	1.95(3)	Zr ₆ -O ₂₇	2.09(2)
Zr ₄ -O ₂₃	1.90(2)	Zr ₅ -O ₃₁	2.29(2)	Zr ₆ -O ₄₂	2.18(2)
Zr ₄ -O ₃₅	2.36(2)	Zr ₅ -O ₄₀	2.20(2)	Zr ₆ -O ₄₄	2.10(3)
Zr ₄ -O ₃₉	2.27(2)	Zr ₅ -O ₄₅	2.16(2)		
Ti ₇ -O ₁₄	1.97(2)	Ti ₈ -O ₁₈	1.97(2)	Ti ₉ -O ₁₆	2.06(2)
Ti ₇ -O ₁₉	2.03(3)	Ti ₈ -O ₂₁	2.13(2)	Ti ₉ -O ₂₈	2.19(3)
Ti ₇ -O ₂₄	1.82(2)	Ti ₈ -O ₃₀	1.80(3)	Ti ₉ -O ₃₆	1.79(3)
Ti ₇ -O ₂₅	1.93(2)	Ti ₈ -O ₃₃	1.88(3)	Ti ₉ -O ₄₅	2.08(2)
Ti ₇ -O ₃₂	2.08(3)	Ti ₈ -O ₃₉	1.94(4)	Ti ₉ -O ₄₆	1.89(4)
Ti ₇ -O ₄₁	1.93(2)	Ti ₈ -O ₄₃	2.05(4)	Ti ₉ -O ₄₇	2.04(3)

shown in Fig. 2a. The broad absorption band around 3400 cm⁻¹ is characteristic of ν_{O-H} vibration of free propanol. The corresponding location of the others bands is reported in Table VI. This spectrum shows intense bands (ν_{asCOO} = 1560 cm⁻¹, ν_{sCOO} = 1448 cm⁻¹ or 1412 cm⁻¹) which are characteristic of acetate groups linked to titanium atoms. The step Δν between ν_{asCOO} and ν_{sCOO} equals 112 or 148 cm⁻¹, respectively if we consider ν_{sCOO} at 1448 cm⁻¹ or 1412 cm⁻¹. Alcock *et al.* (10) have studied many acetate containing compounds and gave Δν between 120 and 200 cm⁻¹ for bridging acetates. Von Thiele and Panse (11) gave Δν = 160 cm⁻¹ as a value for bridging acetate group. Based on these results and on the structural determination, we propose the lowest energy band as ν_{sCOO}. Then, the highest band (1448 cm⁻¹) was attributed to δ_{CH₃}.

The high-energy bands (2964 to 952 cm⁻¹) were associated with the alkyl chains stretching and bending. The band at 660

TABLE V
ENVIRONMENTS OF METALLIC ATOMS
(b: bridging, t: terminal)

	μ ₄ -OXO	μ ₃ -OXO	(OAc)	(OPr) _b	(OPr) _t
Zr ₁	xx	xx	xx	xx	
Zr ₂ -Zr ₃	x	xx	xx	xx	
Zr ₄ -Zr ₅	x	xx	x	xx	x
Zr ₆ -Zr ₇	x	xx	xx	x	
Ti ₈ -Ti ₉	x	xx	x	xx	

cm⁻¹ corresponds to ν_{M-O} and the band at 460 cm⁻¹ to ν_{M-O-M}.

Gel. Figure 2b gives the FTIR spectrum of the gel and Table VI the location of bands. The presence of the characteristic bands of acetate groups linked to metallic atoms (ν_{as} = 1557 cm⁻¹ and ν_s = 1412 cm⁻¹) were noted. The step Δν = 145 cm⁻¹ indicates a bridging coordination mode. The other band assignment is as for the crystals. The existing acetate and propoxy groups in the gel indicate that hydrolysis was not complete.

TABLE VI
INFRARED ABSORPTION BANDS (cm⁻¹) IN
CRYSTALS AND GEL

	Crystals	Gel
Acetate groups		
ν _{asCOO}	1560	1557
δ _{CH₃}	1448	1454
ν _{sCOO}	1412	1412
Propoxy groups		
ν _{C-H}	2964-2874 1340	2931
δ _{C-H}		1345
ν _{C-O}	1260 1122-1027	1162-1028
M-O		
ν _{M-O}	660	663
ν _{M-O-M}	460	480

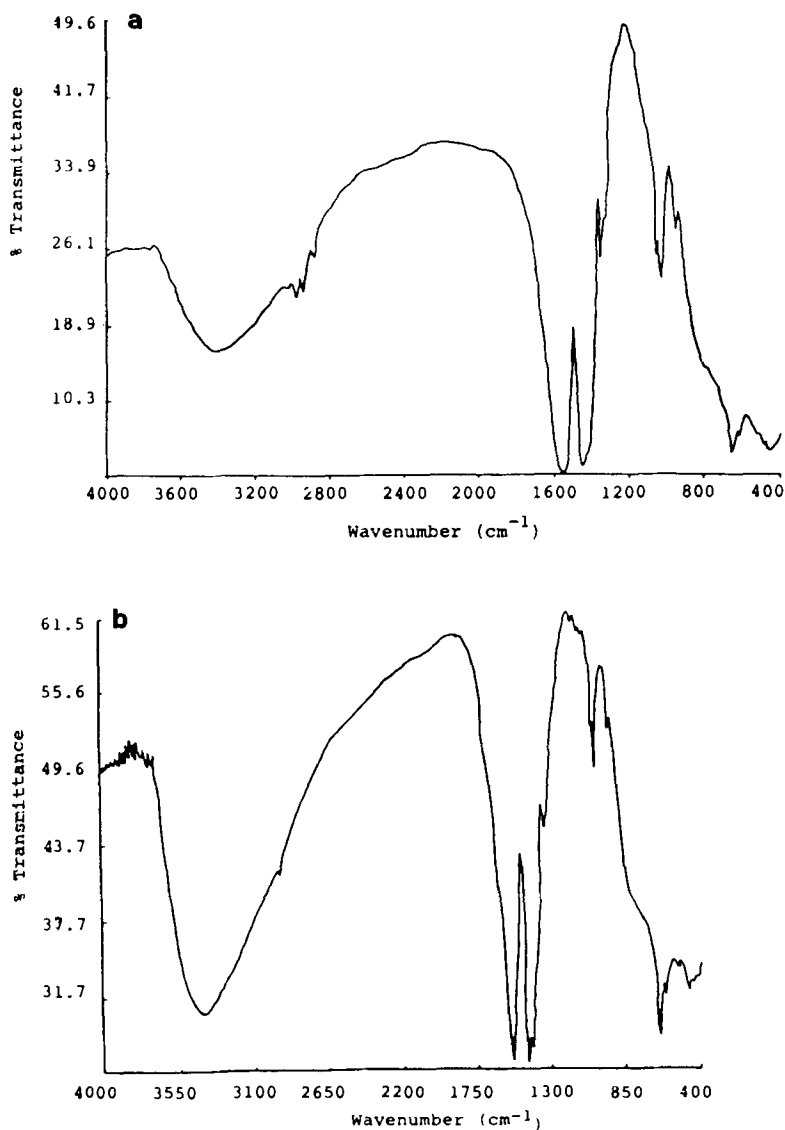


FIG. 2. (a) Infrared spectrum of $Zr_6Ti_3(OPr)_{16}(OAc)_8O_6$ crystals in KBr. (b) Infrared spectrum of the mixed gel.

NMR Spectroscopy

Crystal. ^{13}C NMR spectrum of the crystal $Zr_6Ti_3(O^iPr)_{16}(OAc)_8O_6$ in solid state is given in Fig. 3a. The corresponding location of chemical shifts $\delta^{13}C$ is reported in Table VII.

Two signals were observed in the characteristic field of carbon atoms $\underline{C}H_2$ linked to oxygen atom. The first signal at 63.8 ppm was attributed to carbon atoms in bridging propoxy groups, the second and third at 72.0 and 73.7 ppm correspond to carbon atoms in terminal propoxy or bridging isopropoxy

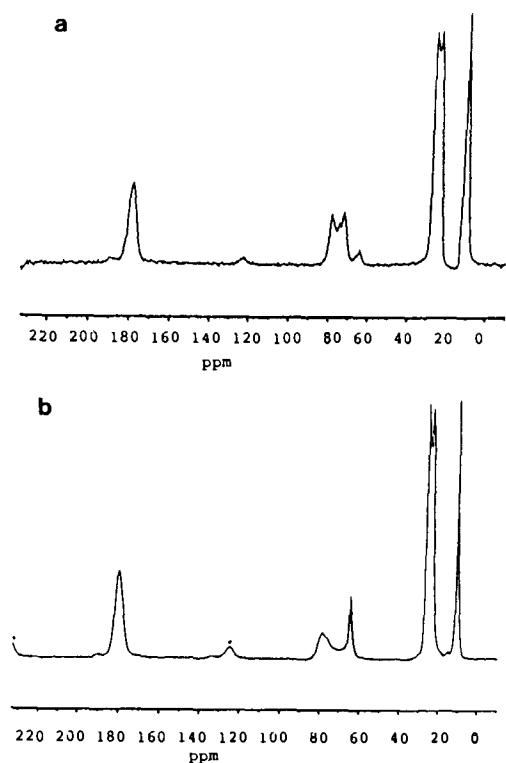


FIG. 3. (a) ^{13}C NMR spectra of solid state $\text{Zr}_6\text{Ti}_3(\text{OPr})_{16}(\text{OAc})_8\text{O}_6$ crystals. (b) ^{13}C NMR spectra of solid state mixed gel (* rotation bands).

groups. The last peak was observed at 78.1 ppm, which should be representative of carbon atom $\underline{\text{C}}\text{H}$ in terminal isopropoxy groups. Consequently, the two types of alkoxy groups might exist in the crystal network. Unfortunately, because of the high thermal agitation factors of terminal carbon atoms, the structural study was not able to confirm this result.

The NMR peak situated at 177.7 ppm corresponds to carbon atoms $\underline{\text{C}}-\text{O}$ of acetate groups.

Gel. The ^{13}C NMR spectrum of the dried gel is given in Fig. 3b. The corresponding $\delta^{13}\text{C}$ shifts are reported in Table VII and are relative to propoxy and acetate groups.

The large peak centered at 78.2 ppm is not clearly defined and does not permit the

location of the various carbon atoms of terminal propoxy and bridging or terminal isopropoxy groups.

Thermal Analysis

Crystal. As indicated in Fig. 4, the thermogravimetric analysis of $\text{Zr}_6\text{Ti}_3(\text{OPr})_{16}(\text{OAc})_8\text{O}_6$ crystals shows a 50% weight loss in air. The theoretical weight loss to obtain oxide form is 55.6%. The two steps centered at 110 and 390°C correspond to the departure of organic groups (PrOH and OR with $R = \text{Pr}$ or Ac). The increasing weight observed between 470 and 660°C might be due to an insertion of oxygen atoms in the lattice. The weight loss between 660 and 700°C is due to residual organic groups departure.

The differential thermal analysis in air (Fig. 4) shows an endothermic stage between 70 and 220°C, which is followed by several exothermic stages. The two first exothermic peaks, centered at 380 and 450°C, are corresponding to the combustion of organic groups (OPr and OAc). The third exothermic peak situated at 640°C is due to residual carbonaceous organic groups combustion. The last exothermic peak observed between 680 and 720°C corresponds to the oxide crystallization. X-ray diffraction pattern confirms this crystallization above 700°C.

TABLE VII

^{13}C NMR CHEMICAL SHIFTS (ppm) OF SOLID-STATE $\text{Zr}_6\text{Ti}_3(\text{OPr})_{16}(\text{OAc})_8\text{O}_6$ CRYSTALS AND GEL

Location	Crystals	Gel
$\underline{\text{C}}\text{H}_3$ group propoxy	10.0	10.2
$\underline{\text{C}}\text{H}_3$ acetate group	23.6	23.6
$\text{CH}_3-\underline{\text{C}}\text{H}_2$ propoxy group	26.3	26.7
$\text{CH}_3-\text{CH}_2-\underline{\text{C}}\text{H}_2$ bridging propoxy group	63.8	64.0
$\text{CH}_3-\text{CH}_2-\underline{\text{C}}\text{H}_2$ terminal propoxy group	72.0	
$\underline{\text{C}}\text{H}$ bridging isopropoxy group	73.7	78.2
$\underline{\text{C}}\text{H}$ terminal isopropoxy group	78.1	
$\underline{\text{C}}-\text{O}$ acetate group	177.7	179.2

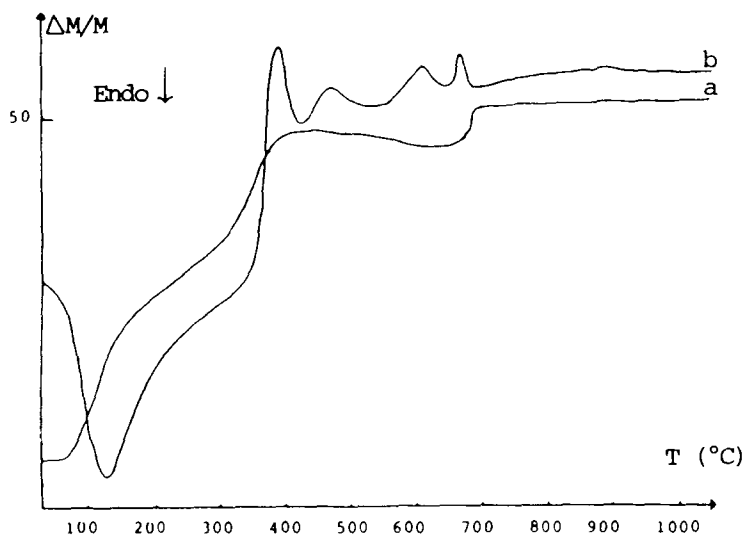


Fig. 4. TGA (a) and DTA (b) curves of $Zr_6Ti_3(OPr)_{16}(OAc)_8O_6$ crystal in air.

In order to distinguish the peaks linked to oxide crystallization and those due to combustion of the organic groups, a thermal study in an inert atmosphere (N_2) was performed. DTA curve shows two endothermic peaks between 70 and 360°C, corresponding to the product decomposition without combustion. No exothermic peak was observed. In fact, the oxide forms slowly until 1000°C; the resulting product was black, due to an oxygen deficiency, and crystallizes as shown by powder X-ray diffraction.

The decomposition of $Zr_6Ti_3(OPr)_{16}(OAc)_8O_6$ crystals has been studied by infrared spectroscopy (Table VIII). As organic

groups were still observed at 640°C, this analysis confirms the DTA results.

Powder X-ray diffraction of $Zr_6Ti_3(OPr)_{16}(OAc)_8O_6$ crystals heat treated at 640°C revealed an amorphous product which became crystalline only above 700°C (Fig. 5). The resulting oxide corresponds neither to the waited oxide mixtures, ($ZrTiO_4 + ZrO_2$) or ($2ZrO_2 + TiO_2$), nor to any other phase listed in tables.

Gel. The TGA curve in Fig. 6, shows the same peaks as the crystals. The three weight losses are relative to the departure of the different organic groups of the polymeric lattice.

The DTA curve (Fig. 6) shows some similarities with crystals one. We observe the same phenomena: an endothermic peak followed by two exothermic peaks corresponding to the decomposition of organic products ($OR = OAc, OPr$) and an exothermic peak centered at 680°C, relative to the crystallization.

Powder X-ray diffraction of the phase obtained when gel was treated at 750°C leads to zirconium titanate $ZrTiO_4$ (Fig. 7). This

TABLE VIII
INFRARED SPECTROSCOPY RESULTS
DURING CRYSTAL DECOMPOSITION

	C-H	C-O
200°C	Yes	Yes
450°C	Yes	Yes
640°C	Yes	No

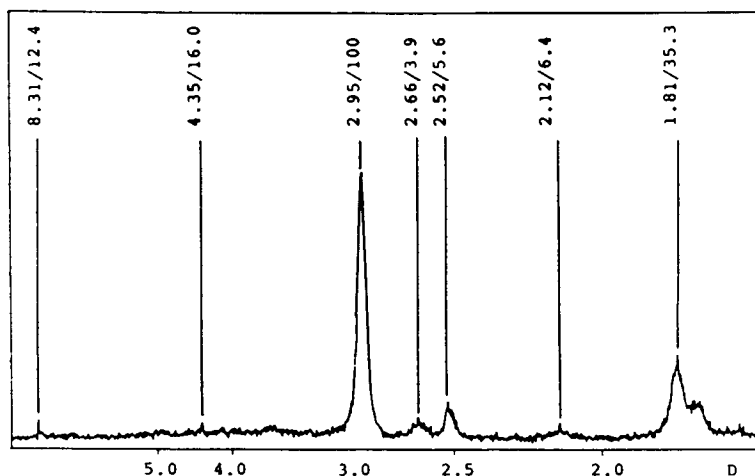


FIG. 5. X-Ray diffraction pattern of $Zr_6Ti_3(OPr)_{16}(OAc)_8O_6$ crystals treated at $700^\circ C$.

indicates that stoichiometry is conserved in the gel; in contrast, the crystal lattice is formed by 6 Zr atoms and 3 Ti atoms.

Discussion and Conclusion

The crystal $Zr_6Ti_3(OPr)_{16}(OAc)_8O_6$ was obtained from two alkoxide precursors:

one was a monomer $Ti(O^iPr)_4$ and the other one was an oligomer $Zr(O^nPr)_4$. The structure of titanium and zirconium alkoxides depends on their oxidation state (4) and on their tendency to increase their coordination number (6 is the maximum for Ti atoms and 8 for Zr atoms). Alkoxides can increase in size by forming alkoxy

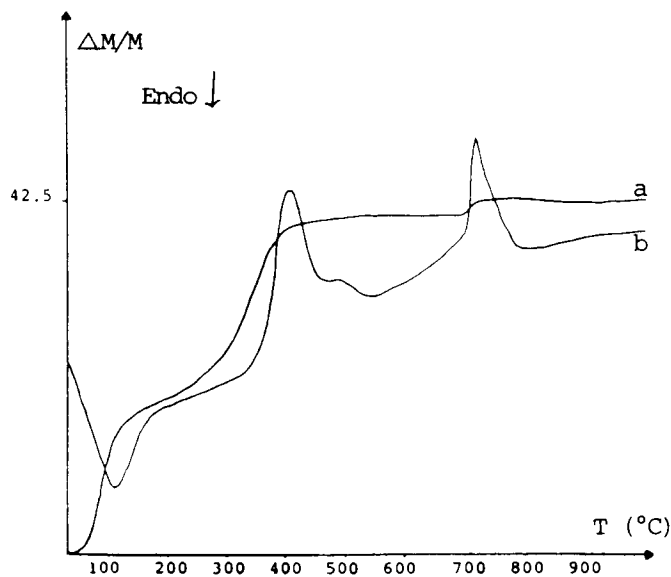


FIG. 6. TGA (a) and DTA (b) curves of mixed gel in air.

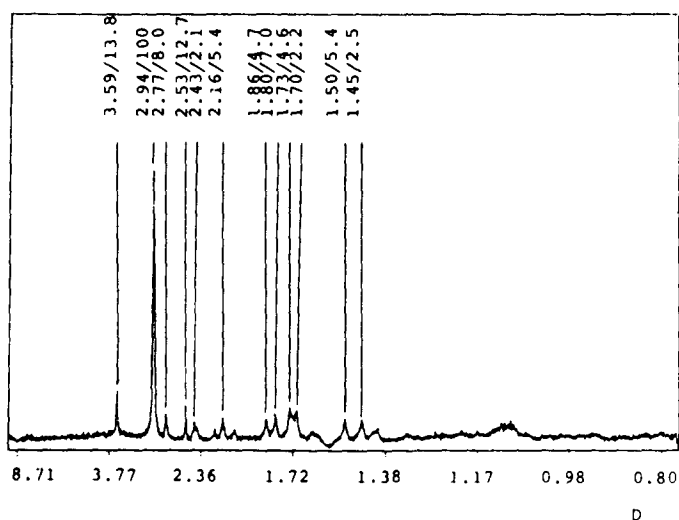
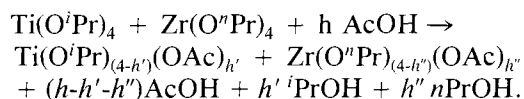


FIG. 7. X-Ray diffraction pattern of mixed gel treated at 750°C.

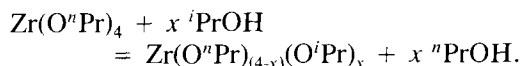
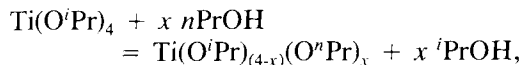
(OR) bridges if not blocked by steric hindrance.

The alkoxide reactivity can be controlled by chemical modification of alkoxide molecules (7). The most common compound used in sol-gel modification is acetic acid. This allows an increase of the metallic atoms coordination by formation of acetate bridges (12), and also a control of the alkoxide hydrolysis. The chemical modification of alkoxides by AcOH has been studied in several publications (7, 13–15). The results presented in this paper confirm previous researches. The different reactions which occur when hydrolyzing a mixture of the two Ti and Zr alkoxides by esterification reaction are:

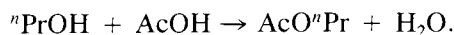
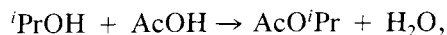
- Modification of $\text{Ti}(\text{O}^i\text{Pr})_4$ and $\text{Zr}(\text{O}^n\text{Pr})_4$ by acetic acid:



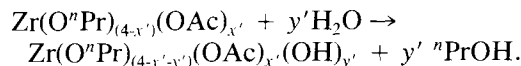
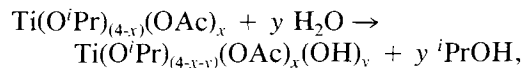
- Exchange reaction between the two alkoxy groups:



- Esterification of the two alcohols:



- Hydrolysis of isopropoxy and propoxy groups and substitution by hydroxo groups:



- Condensation by alcoxolation or oxolation initiated by hydroxo groups and formation of μ -oxo bridges: Ti–O–Zr, Zr–O–Zr, and Ti–O–Ti.

The IR and ^{13}C NMR spectra demonstrate that the ligands surrounding the metal atom are identical in crystals and gels. The structure described in this paper $\text{Zr}_6\text{Ti}_3(\text{OPr})_{16}$

(OAc)₈O₆ shows the effect of acetic acid which act as bidentate ligand. The coordination of metallic elements varies from 6 to 8 depending on their environment.

These results allow us to highlight the similarity between gel and crystal structures. The structure of molecular clusters determined in the crystals may be representative of the structure of the intermediate species formed during gelation.

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