Nonhydrolytic Sol−Gel Routes to Oxides

A. Vioux

Université Montpellier II, Sciences et Techniques du Languedoc, case 007, Place E. Bataillon, F 34095 Montpellier Cedex 5, France

Received May 7, 1997. Revised Manuscript Received August 11, 1997[⊗]

This review surveys the chemistry of various nonhydrolytic sol−gel processes including hydroxylation in nonaqueous systems and aprotic condensation reactions. Some examples of applications in the field of single and multicomponent oxides demonstrate the interest of these approaches as alternatives to the usual hydrolytic routes. More particularly nonhydrolytic methods lead to improved control over the molecular level homogeneity and stoichiometry of multicomponent oxides.

1. Introduction

Beyond the control of the composition and the processing of materials, the development of low-temperature routes to materials aims to allow the control of their microstructure. Particulary important is to tailor advanced materials at the atomic level for specific applications, such as microelectronics, separation science and catalysis. In sol−gel methods, which are based on the hydrolysis−condensation of molecular precursors, such as metal alkoxides, the major problem is to control the reaction rates which are generally too fast, resulting in loss of microstructural control over the final oxide material.[1] An attractive solution is to use organic additives which act as chelating ligands (carboxylic acids, β-diketones, etc.) and modify the reactivity of the precursors.[2] One alternative strategy is provided by *nonhydrolytic* sol−gel processes, in which precursors, solvent, experimental conditions, catalysts, and reaction mechanisms are changed.[3,4]

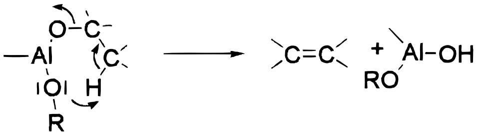
This paper shortly presents in the first part the molecular chemistry on which nonhydrolytic processes are based. Then details are given on the early applications in the field of single oxides (titania and alumina). The capabilities of the nonhydrolytic approach in the field of mixed oxides (silicates and titanates) are discussed in the last section.

2. Molecular Chemistry of Nonhydrolytic Sol−Gel Processes

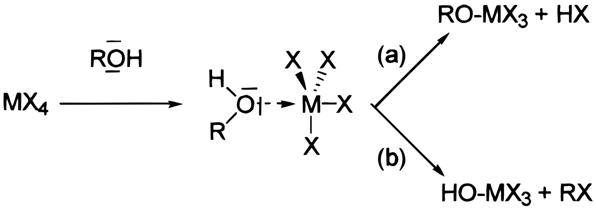
Discarding reactions where water is produced in situ,[3] nonhydrolytic sol−gel methods fall into two groups, depending on whether they involve hydroxylation reactions or not. In the latter case rigorously aprotic conditions are preserved by the use of heterofunctional condensation reactions excluding hydroxyl groups; such reactions will be referred to as aprotic condensation reactions.

2.1. Nonhydrolytic Hydroxylation Reactions. A simple method is the thermal decomposition of metal alkoxide (carboxylate) precursor (in the temperature range 200−300 °C), where hydroxyl groups are produced via a cyclic elimination mechanism with liberation of alkene (Scheme 1).[5] This reaction type is more relevant to MOCVD (metal−organic chemical vapor deposition), but it is most likely involved in the thermal degradation of residual alkoxy groups during the calcination of nonhydrolytic gels into oxides.[6]

Scheme 1



Scheme 2



Another nonhydrolytic hydroxylation method is provided by the action of certain alcohols on halides. Thus, while reaction of primary and secondary alcohols with tetrachlorosilane is the usual method for preparing tetraalkoxysilanes,[7] the same reaction with tertiary alcohols and benzylic alcohols afford silica and the corresponding alkyl halide, RCl.[8,9] The two modes of reaction involve initially the coordination of a lone pair of electrons of an alcoholic oxygen atom to the silicon center, followed by the cleavage of either the hydroxyl or alkoxyl group (Scheme 2).[10] Electron-donor substituent groups in the alkyl radical direct the process to hydroxylation (pathway b; liberation of RCl) by favoring the nucleophilic attack of chloride on the carbon group, due to its increased cationic character (for arguments for an S_N1 mechanism see ref 8). This pathway is also illustrated by the reaction of *tert*-butyl alcohol on titanium tetrachloride, which leads, at room temperature, to a compound of empirical formula $Ti(OBu^t)_{0.127}(OH)_{3.19}Cl_{0.68}$ (based on elemental and thermogravimetric analyses)[11]

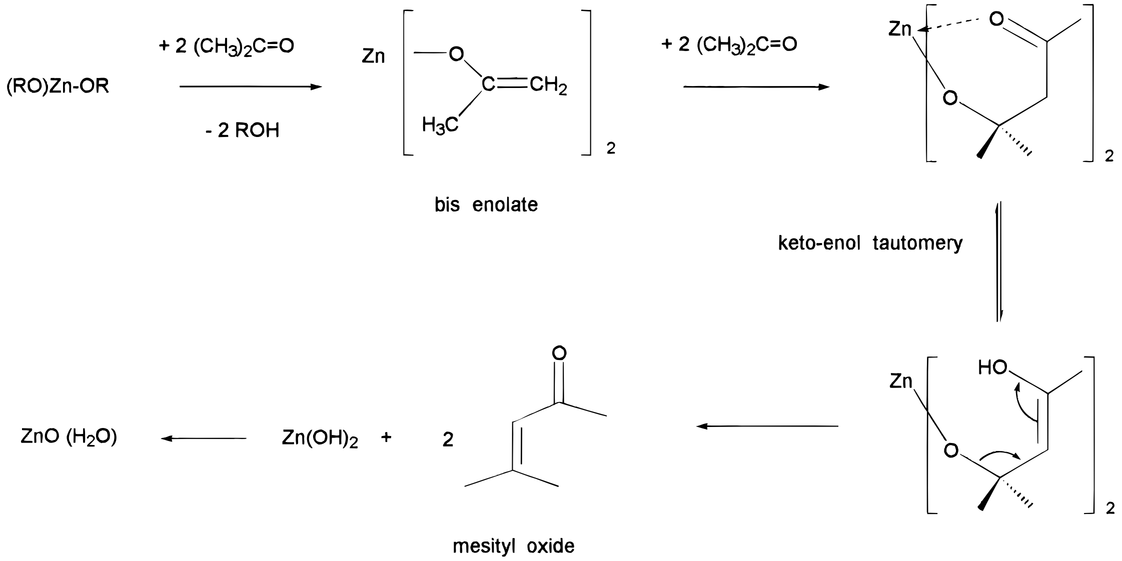
Another interesting method of nonhydrolytic hydroxylation is the reaction of carbonyl compounds such as ketones with *basic* metal alkoxides, which are able to induce ketolization. Thus, the reaction of acetone with zinc(II) alkoxide resulted in formation of a gel, ulti-

---

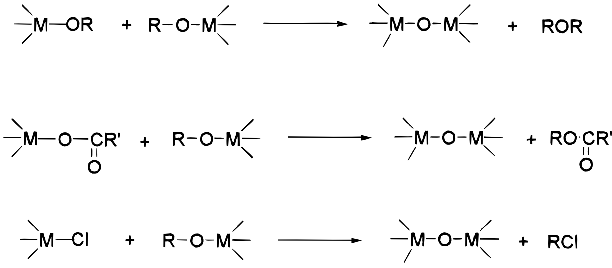
[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1997.

S0897-4756(97)00322-0 CCC: $14.00

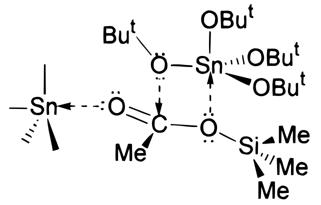
Scheme 3



Scheme 4



Scheme 5



mately liberating zinc oxide, the alcohol, and mesityl oxide via the decomposition of the intermediate bisketolate complex (Scheme 3).[12]

2.2. Aprotic Condensation Reactions. An attractive nonhydrolytic method for the formation of an oxo bridge is provided by the condensation reaction between two different functional groups bonded to two different metal centers by eliminating a small organic molecule, as featured in Scheme 4. Although ether elimination has been postulated in the formation of some μ-oxoalkoxides,[13,14] it has not been developed so far as sol–gel processing, unlike the two other ways, ester and alkyl halide eliminations.

2.2.1. Ester Elimination. The condensation reaction between metal or silicon acetates and metal alkoxides has been used for the preparation of various metal trimethylsilyloxides $M(OSiMe_3)_n$ (M = Ti, Zr, $n = 4$; M = Nb, $n = 5$)[15] and polymetallic oxo clusters.[13,14] It has also been successfully applied to the preparation of ZrO_2 (from a mixture of $Zr(OPr^n)_4$ and $Zr(OAc)_4$) and homogeneous TiO_2–SiO_2 and ZrO_2–SiO_2 binary oxides (the latter will be detailed in section 4).[16,17]

Hampden-Smith and co-workers[18–21] have recently rationalized the factors governing the ester elimination in the reactions between tin(IV) tetra-*tert*-butoxide and various acetates, such as $Pb(OAc)_4$, $Sn(OAc)_4$, and $Me_3Si(OAc)$. From experiments employing ^{17}O-labeled $Sn(OBu^t)_4$, they have proposed a mechanism derived from acid-catalyzed transesterification (Scheme 5):[20] coordination of the carbonyl oxygen of the acetate to a tin center decreases the electron density at the carbonyl carbon, allowing for nucleophilic attack of the oxygen. Accordingly the ability of a coordinating solvent, such as pyridine, to compete successfully with the carboxylate ligand for the vacant coordination site at tin, may explain that in this solvent the reaction resulted in the only ligand-exchange products. Therefore the authors have defined a set of criteria required to ensure the success of ester elimination reactions:[20,21] (i) a nonchelating carboxylate ligand, (ii) noncoordinating solvent, (iii) an electropositive metal alkoxide, and (iv) vacant coordination sites on the metal alkoxide center.

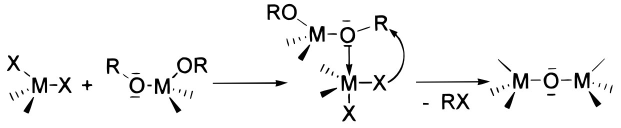
An interesting extension of this route would be to generate the acyl groups in situ. However the two-component systems comprising alkoxides and carboxylic acids (the latter serving as solvent) induce the removal of alcohol and the subsequent water-generating esterification reaction.[22] Another possibility would be the direct reaction of anhydride with alkoxide precursors:

$$M(OR)_n + n/2(R'C{=}O)_2OMO_{n/2} + nR'COOR$$

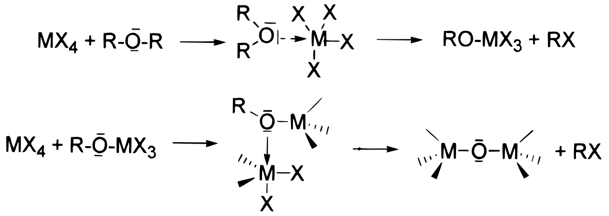
However, in the case of titanium, this process has been found to be mediocre, the reaction of acetic anhydride with $Ti(OPr^i)_4$ hardly occurring at 140 °C (Pr^i = isopropyl) and only in the presence of a Lewis acid catalyst such as $TiCl_4$.[11]

2.2.2. Alkyl Halide Elimination. As for ester elimination, alkyl halide elimination occurs in the temperature range from room temperature to about 100 °C, depending on the reagents involved.[9,23] The condensation between alkoxide and halide functions is outlined in Scheme 6.[24] An alkoxy group coordinates to the metal center of a second molecule; then the release of an alkyl halide molecule leads to an oxide linkage. This reaction results in the nucleophilic cleavage of an OR bond, and, therefore, the electronic effects on the carbon center are

Scheme 6



Scheme 7



expected to be critical. Thus, with silicon, this reaction works only with tertiary and benzylic carbon groups, which are able to stabilize a carbocation.[9,25]

Interestingly alkoxy groups may be produced in situ by the alcoholysis or the etherolysis of metal halides.[6,9,26] Scheme 7 depicts the likely two-step process of these reactions:

(i) The formation of alkoxy groups involves the coordination of the organic oxo compound with the metal center; followed by the liberation of hydrogen halide or alkyl halide.

(ii) The subsequent condensations proceed through the same pathway as given in Scheme 6.

The etherolysis of metal chlorides (usually with diethyl or diisopropyl ether) offers a versatile sol−gel route to transition-metal oxides (V, Ti, Zr, Nb, W, etc.),[27] which is all the more interesting since transition-metal halides are more available than the parent alkoxides. It is well worth noting that hexamethyldisiloxane ($(\mathrm{Me_3Si})_2\mathrm{O}$) may be used as oxygen donor instead of ether; in this case the formation of metal oxide occurs through the release of $\mathrm{Me_3SiCl}$.[28]

Note that the stoichiometry requires an equal number of alkyl groups and halide groups. Thus, the idealized equations of the reactions corresponding to the preparation of mixed oxide gels with different M/M′ ratios are

$$x\mathrm{MX}_n + y\mathrm{M'X}_{n'} + {}^1/_2(nx + n'y)\mathrm{ROR} \rightarrow \mathrm{M}_x\mathrm{M'}_y\mathrm{O}_z + (nx + n'y)\mathrm{R{-}X}$$

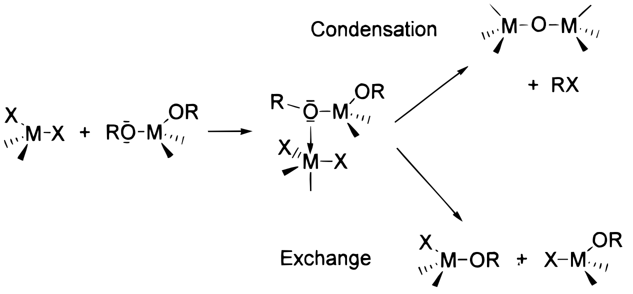
where $z = {}^1/_2(nx + n'y)$ and

$$t\mathrm{MX}_n + u\mathrm{M'X}_{n'} + v\mathrm{M(OR)}_n + w\mathrm{M'(OR)}_{n'} \rightarrow \mathrm{M}_x\mathrm{M'}_y\mathrm{O}_z + (nt + n'u)\mathrm{R{-}X}$$

where $z = {}^1/_2(nt + n'u) = {}^1/_2(nv + n'w)$, and $x = t + v$, $y = u + w$.

Further insights into the solution chemistry of the alkyl halide elimination has been recently given by a study of the etherolysis−condensation of titanium tetrachloride with diisopropyl ether ($\mathrm{Pr}^i{}_2\mathrm{O}$), and the direct condensation between $\mathrm{TiCl_4}$ and titanium tetraisopropoxide.[29] The main reaction that takes place at room temperature in mixtures of $\mathrm{TiCl_4}$ and $\mathrm{Ti(OPr}^i)_4$ is the redistribution of OPr^i and Cl ligands. In the presence of $\mathrm{Pr}^i{}_2\mathrm{O}$, the alkoxylation of $\mathrm{TiCl_4}$ leads in a few minutes to the formation of $\mathrm{Ti(OPr}^i)\mathrm{Cl_3}$; the second alkoxylation step is much slower and is not completed when condensation starts. Thus, the true precursors in both nonhydrolytic routes (alkoxide or ether) are titanium chloroisopropoxides species Ti $\mathrm{Cl}_{4-i}(\mathrm{OPr}^i)_i$ in equilibrium:

Scheme 8



$$2\mathrm{TiCl}_{4-i}(\mathrm{OPr}^i)_i \rightleftharpoons \mathrm{TiCl}_{5-i}(\mathrm{OPr}^i)_{i-1} + \mathrm{TiCl}_{3-i}(\mathrm{OPr}^i)_{i+1}$$

Note that the first step of the ligand-exchange mechanism[30] featured in Scheme 8 is similar to the first step of the condensation mechanism (Scheme 6); thereafter the cleavage of the oxygen−metal bond instead of the carbon−oxygen one in the intermediate Lewis adduct leads to the exchange reaction. Moreover one has to bear in mind that some titanium chloroisopropoxides are in oligomer form due to the trend of the metal center to expand its coordination through alkoxy bridges.[29]

In both cases (etherolysis or direct condensation) the condensation reaction is slow at room temperature, and it takes place at 100 °C after an induction period. A conspicuous feature in the curves displaying the extent of the condensation against the time (Figure 1)[29] is the strong dependence of the induction period needed to initiate the condensation on the initial OPr^i/Ti ratio. Thus when OPr^i/Ti increases from 1 to 2.3, the induction time grows from 0.2 h to more than 300 h at 100 °C. This cannot be accounted for by the variation of concentration in OPr^i or Cl groups; this behavior has to be related to the drastic effect of the OPr^i/Ti ratio on the relative concentrations of the $\mathrm{TiCl}_{4-i}(\mathrm{OPr}^i)_i$ species. Actually Weingarten and Van Wazer[31] previously found that the heats of redistribution for the $\mathrm{TiCl_4/Ti(OPr}^i)_4$ system were strongly exothermic, indicating a large deviation from random scrambling (since randomness is achieved when equilibria are entirely entropy controlled).[30] An evaluation of the equilibrium constants:

$$K_{\mathrm{i}} = \frac{[\mathrm{TiCl}_{5-i}(\mathrm{OPr}^i)_{i-1}][\mathrm{TiCl}_{3-i}(\mathrm{OPr}^i)_{i+1}]}{[\mathrm{TiCl}_{4-i}(\mathrm{OPr}^i)_i]^2} \qquad i = 1, 2, 3$$

based on their data gives values of about 10^{-4}. Therefore a rough estimation indicates that, when $\mathrm{OPr}^i/\mathrm{Ti} = 2$ in the alkoxide route, the main precursor is by far $\mathrm{Ti(OPr}^i)_2\mathrm{Cl_2}$, the concentrations of $\mathrm{Ti(OPr}^i)_3\mathrm{Cl}$ and $\mathrm{Ti(OPr}^i)\mathrm{Cl_3}$ are on the order of 1%, and there is virtually no more $\mathrm{TiCl_4}$ and $\mathrm{Ti(OPr}^i)_4$. Accordingly, the key species appears to be $\mathrm{Ti(OPr}^i)\mathrm{Cl_3}$; the lower its concentration, the higher the induction time. Thus the extremely long induction time observed when $\mathrm{OPr}^i/\mathrm{Ti} = 2.3$ shows that $\mathrm{Ti(OPr}^i)_2\mathrm{Cl_2}$ and $\mathrm{Ti(OPr}^i)_3\mathrm{Cl}$ are practically inert toward condensation in the absence of $\mathrm{Ti(OPr}^i)\mathrm{Cl_3}$. Conversely, the decrease in the induction time observed when $\mathrm{OPr}^i/\mathrm{Ti} = 2$ ($t_{\mathrm{ind}} \approx 7$ h) shows that $\mathrm{Ti(OPr}^i)_2\mathrm{Cl_2}$ is much more reactive in the presence of a small amount of $\mathrm{Ti(OPr}^i)\mathrm{Cl_3}$. Moreover the shorter induction time observed in the etherolysis route ($t_{\mathrm{ind}} \approx$

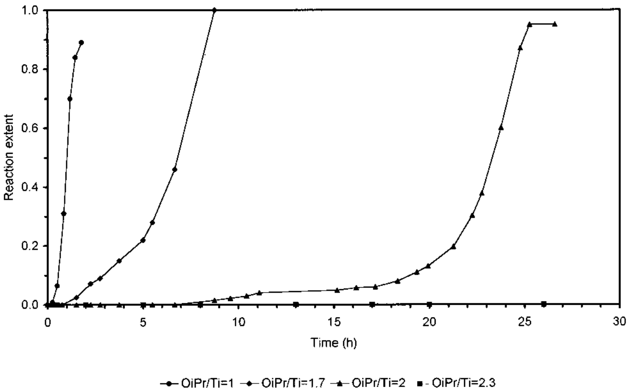
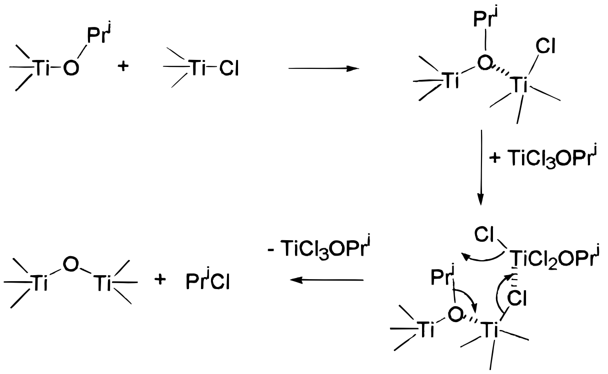


Figure 1. Condensation extent at 100 °C in mixtures of titanium tetrachloride and titanium tetraisopropoxide in chloroform of various overall OPr^i/Ti ratios.

Scheme 9



3 h) may be attributed to the fact that the actual OPr^i/Ti ratio in the chloroisopropoxides mixture is lower than 2 when the condensation starts (the alkoxylation being incomplete), so that the equilibrium concentration of Ti(OPr^i)Cl$_3$ is higher than in the equimolar mixture of TiCl$_4$ and Ti(OPr^i)$_4$.

This behavior suggests that during the induction process the first condensations between Ti−Cl and Ti−OPr^i functions are efficiently catalyzed by Ti(OPr^i)Cl$_3$. As a matter of fact, the nonhydrolytic condensation between Si−Cl and Si−OR bonds is known to be catalyzed by Friedel−Crafts catalysts, such as FeCl$_3$ or AlCl$_3$.[32,33] Ti(OPr^i)Cl$_3$ is known as a strong Lewis acid, able to form 1:2 adducts with a variety of Lewis bases.[34,35] In addition, it has been shown that Ti(OPr^i)Cl$_3$ is a very active catalyst for the polymerization of olefins, whereas Ti(OPr^i)$_2$Cl$_2$ is inactive.[36]

Another interesting point is the sigmoid shape of the curves in Figure 1. Such behavior suggests that the condensation is catalyzed by the reaction products. However, the condensation rate was not modified when the reaction was performed in the presence of a titania precipitate or in the presence of isopropyl chloride, which are the final products of the condensation. Thus, the sigmoid shape indicates that the intermediate oxochloroisopropoxide species are much more reactive toward condensation than the starting chloroisopropoxides, possibly because they are better Lewis acids. As a matter of fact, titanium oxychloride, TiOCl$_2$, is an even more active catalyst for the polymerization of olefins than Ti(OPr^i)Cl$_3$.[36]

One suggested mechanism is that a Lewis acid species (for instance, Ti(OPr^i)Cl$_3$) catalyzes the conversion of alkoxo bridges (for instance, in the Ti(OPr^i)$_2$Cl$_2$ oligomers) to oxo bridges by activation of a Ti−Cl bond (Scheme 9).[29]

3. Applications to the Preparation of Single Oxides

3.1. Titania. Titania samples prepared by different nonhydrolytic sol−gel methods have been found to vary in structure and texture (Table 1).[11] Thus, the reaction of diethyl ether with TiCl$_4$ at 110 °C affords anatase, which begins to convert into rutile only around 950 °C. The reaction of TiCl$_4$ with ethanol leads to rutile as early as 110 °C, whereas the reaction of tertiary butanol at 110 °C leads to the formation of brookite, which is a quite uncommon phase in synthetic products.[37] These results highlight the capability of nonhydrolytic sol−gel methods to obtain a particular crystalline structure by varying the nature of the oxygen donor (ether or alcohol), as do conventional sol−gel methods by controlling the hydrolysis conditions.

The experimental conditions (a prolonged heat treatment in a sealed glass tube near 110 °C) are suggestive of a *solvothermal* treatment. Thus the effect of the alcoholic medium on crystallization is most plausible. The ability of alcohol to cleave Ti−O−Ti linkages (thus slightly reversing the condensation reaction) may be invoked.[38] However the formation of brookite with tertiary alcohols, as well as the early crystallization of rutile in the samples arising from the alcoholysis of TiCl$_4$ with ethanol, are difficult to rationalize. In addition to the effect of the alcoholic medium, the crystallization behavior is most likely influenced by the initial ultrastructure of the amorphous solid, which is determined in each case by the kinetics of the condensation reactions.[29]

3.2. Alumina. The preparation of aluminas that are different in structure and texture depending the nonhydrolytic sol−gel route well illustrates again the tractability of these methods. Thus, the thermal decomposition of aluminum isopropoxide in inert organic solvent at 300 °C (nonhydrolytic hydroxylation) yielded a product consisting of agglomerates of 4−20 nm particles having the χ-alumina structure.[39] Interestingly, the χ-alumina structure was stable and maintained a surface area above 100 m^2/g until its transformation to α-alumina at 1150 °C.

Alumina gels have been prepared by the aprotic condensation of aluminum halides AlX$_3$ (X = Br, Cl) with aluminum alkoxides Al(OR)$_3$ (R = alkyl), around 100 °C.[6] The alumina obtained after drying was amorphous and nonhydrated. An additional heat treatment at 650 °C in air was needed to reduce residual carbon and halogen contents. However the solids remained amorphous after calcination, and kept a specific surface area higher than 200 m^2/g to about 900 °C. Solid-state ^{27}Al NMR spectroscopy (Figure 2) indicated a large amount of 5-fold coordinated aluminum ($^{[5]}$Al) sites in the dried gels, which may be regarded as structural defects giving an explanation for the delayed crystallization. Thus, the $^{[5]}$Al sites disappeared after heating for 5 h at 850 °C, when γ-Al$_2$O$_3$ crystallized. Five-coordinate Al sites are quite unusual in aluminas and might be of interest in the area of catalysis.

Moreover, it is worth noting that pentacoordinate Al sites were evidenced in the initial solution, and therefore

Table 1. Comparison of Different Nonhydrolytic Sol−Gel Routes to TiO_2

oxygen donor	reagents	gel time, h (temp, °C)	byproduct	$\Delta m/m$ (%) based on TGA	RXD after drying at 180 °C	RXD after calcination at 950 °C	S (m^2/g) after calcination at 500 °C
alkoxide	$TiCl_4/Ti(OPr^i)_4$, no solvent	≈5 h (110)	Pr^iCl	−14	amorph + anatase	anatase 100%	160
alkoxide	$TiCl_4/Ti(OBu^t)_4$, toluene	≈0.5 h (110)	Bu^tCl	−19	amorph + anatase	anatase 100%	64
ether	$TiCl_4/2Pr^i_2O$, no solvent	≈3 h (110)	Pr^iCl	−16	anatase	anatase 86%, rutile 14%	120
ether	$TiCl_4/2Et_2O$, no solvent	≈17 h (110)	EtCl	−22	anatase	anatase 42%, rutile 58%	45
alcohol	$TiCl_4$/excess Pr^iOH, $c = 1.8$ mol/L	≤6 h (110)	Pr^iCl	−7	anatase	anatase 37%, rutile 63%	30
alcohol	$TiCl_4$/excess EtOH, $c = 1.8$ mol/L	≤6 h (110)	EtCl	−4	rutile	rutile 100%	10
alcohol	$TiCl_4$/excess Bu*t*OH, $c = 1.8$ mol/L	≤1 h (110)	Bu^tCl	−4	brookite + rutile	rutile 100%	23

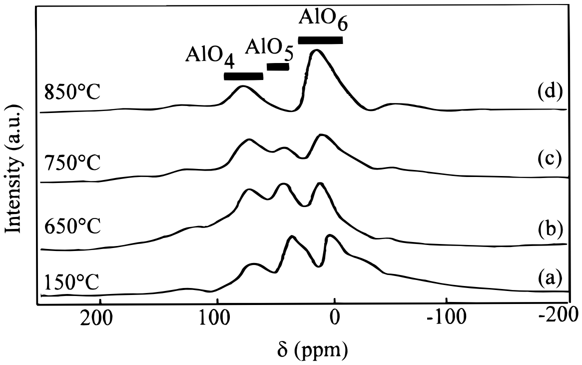
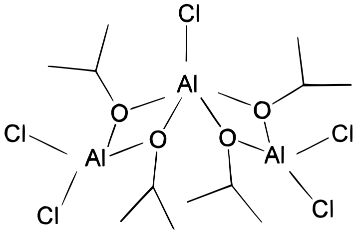


Figure 2. ^{27}Al MAS NMR spectra of the nonhydrolytic gel arising from $Al(Pr^i)_3/AlCl_3$ system as obtained at 150 °C (a), after calcination for 5 h in air at 650 °C (b), and after an additional heating at 750 °C (c) and 850 °C (d).

Scheme 10

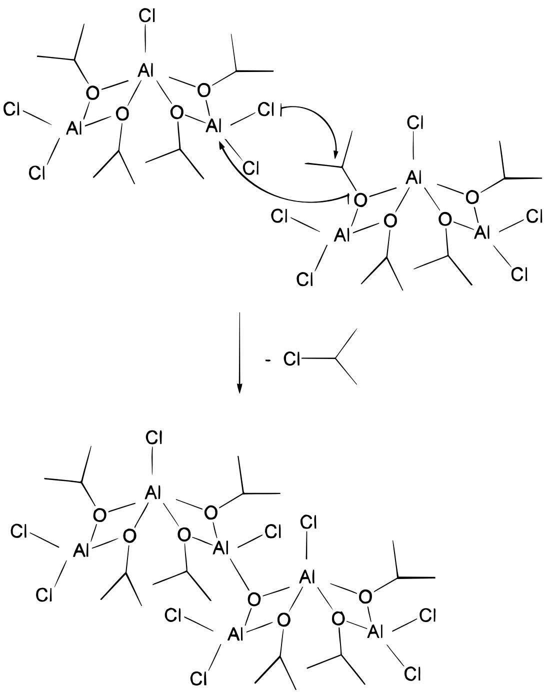


the presence of $^{[5]}$Al sites in the gels might be directly related to the structure of precursors in solution.[40] As in the case of titanium, the true precursors are the aluminum chloroalkoxides formed by ligand-exchange reactions, as in the following example:

$$Al_2Cl_6 + 2Al(OPr^i)_3 \rightarrow AlCl(OPr^i)_2 + Al_3Cl_5(OPr^i)_4$$

In this particular case, other authors[41] have isolated crystals and have given X-ray diffraction evidence for the structure of trimeric $Al_3Cl_5(OPr^i)_4$, which involves one $^{[5]}$Al atom in the center bonded to two tetrahedral aluminum ($^{[4]}$Al) atoms by four alkoxy bridges (Scheme 10). The maintenance of the five-coordinate aluminum sites throughout the gelation supports the belief that the alkoxy bridges are not broken during the aprotic condensation which results from nucleophilic attack of the chloride on the carbon center adjacent to the oxygen atom (Scheme 11).

Scheme 11



4. Applications to the Preparation of Binary Oxides

4.1. General Considerations. The potential advantage of sol−gel processing to multicomponent oxides over conventional mixed powder methods lies in the improved homogeneity expected. In comparison with solid-state reaction, where the migration of ions to interfaces−grain boundaries involves a complete disruption of the structure, the solution reaction of molecular precursors (salts or metal alkoxides) typically involves the breaking of *one* bond and the formation of another, sometimes simultaneously. Thus, even though the reaction between solids requires considerable energy to overcome the lattice energy (typical reaction temperatures in oxide chemistry are in the range 500−2000 °C), sol−gel reactions between components mixed in solution on the molecular scale occurs at low temperatures, thus avoiding phase separation. A high degree of homogeneity in muticomponent glasses may be expected consequently either to delay the crystallization of single oxides or to bring forward the crystallization of one stable mixed oxide, if it exists (on the contrary, a heterogeneous gel containing M−O−M bounded domains would easily lead to the crystallization of M oxide).

However the control of the composition and homogeneity in multicomponent oxide gels is nowhere near as straightforward owing to the different reactivities of various precursors toward hydrolysis and condensation, especially in the case of silicon and metal alkoxides. These differences were attenuated either by prereacting the slower precursor (silicon alkoxide) or by chelating the fast precursor (metal alkoxide).[1] In some cases heterometallic alkoxides (yet containing M−O−M′ bonding) were used. In this view aprotic condensation reactions appear interesting if one remembers the spontaneous formation of mixed-metal complexes from mixtures of some alkoxides, carboxylates, and β-diketonates precursors. However, owing to the above-mentioned rapid ligand-exchange reactions, nonhydrolytic condensation reactions cannot lead to the formation of M−O−M′ bridges with a perfect alternation of the metal centers M and M′. Homogeneity is expected again to depend on the relative rate of self-condensation (M−O−M and M′−O−M′ bridges) toward cross-condensation (M−O−M′ bridges). If extensive self-condensation reactions occur, binary nonhydrolytic gels will be heterogeneous; but if all the reaction rates are of the same order, homogeneity, i.e., a random distribution of the MOM, MOM′, and M′OM′ bridges, will be achieved.

Actually, the limitation of aprotic condensation between metal precursors most often arises from the insolubility of metal carboxylates and halides in organic solvents ($CrCl_3$, $CoCl_2$, $CuCl_2$, etc.). On the other hand, silicon is a special case. Whereas silicon acetates are good candidates toward ester elimination (carboxylate ligands being monodentate toward silicon), silicon chloroalkoxides exhibit a poor reactivity toward alkyl halide elimination, which was found limited to carbon groups activated by electronic effects, such as benzyl groups. Nevertheless, alkyl halide elimination can be efficiently catalyzed by Lewis acids (as mentioned above).[30,31] In that case the question arises as to what extent the presence of high contents of Lewis acid catalysts (that may be released in situ as shown in the case of titanium) is able to level the rates of self- and cross-condensations.

4.2. Silicates. In this respect the study of gels with $3Al_2O_3,2SiO_2$ composition is of particular interest, since the crystallization process of pre-mullite gels is known to be fundamentally affected by microstructure, giving an accurate insight into the scale of mixing between aluminum and silicon.[42] Thus the formation of pseudo-tetragonal mullite as early as 980 °C, which was reported for a gel obtained by etherolysis of a mixture of $SiCl_4$ and $AlCl_3$, is indicative of a chemical homogeneity at the atomic level.[43,44] Moreover the ^{29}Si solid-state MAS NMR study of the samples calcined at 900 °C (that is just before crystallization) confirmed this point. A broad signal was observed at ca. −90 ppm, which substantiated the occurrence of Si−O−Al bonding, considering that this signal corresponded to the overlap of the different contributions of the five possible tetrahedral environments at silicon: $Si[(OSi)_4]$ (ca. −109 ppm), $Si[(OAl)(OSi)_3]$ (ca. −102 ppm), $Si[(OAl)_2(OSi)_2]$ (ca. −96 ppm), $Si[(OAl)_3(OSi)]$ (ca. −90 ppm) and $Si[(OAl)_4]$ (ca. −86 ppm).

Well-condensed, monolithic gels with various compositions SiO_2-TiO_2 and SiO_2-ZrO_2 have been prepared by the aprotic condensation between chloride and isopropoxide functions at 110 °C.[45] The Si/M ratio of the final oxide was controlled by the composition of the starting mixture.

Concerning the SiO_2-TiO_2 gels, infrared spectroscopy indicated the presence of a limited number of Si−O−Ti bonds after calcination for 5 h at 500 °C.[45] However the sample within the stable glass region (5 mol % Ti) appeared perfectly homogeneous: it crystallized at 900 °C as single-phase cristobalite oxide, with Ti^{4+} ions substituting Si^{4+} ions at random. On the other hand, the precipitation of anatase was observed for the Si−Ti oxides with a high Ti content (20−50 mol % Ti), which are outside the stable glass region. However the transformation of anatase to rutile was not observed, even after 2 h at 1300 °C.[46] Note that Iwasaki et al. had previously reported that the reaction of $Ti(AcAc)(OPr^i)_3$ with $Si(OAc)_4$ in tetrahydrofuran had led to nonhydrolytic SiO_2-TiO_2 gels, in which a high degree of homogeneity had been inferred from the delayed crystallization tendency (assuming that a heterogeneous gel with Ti−O−Ti bonds would have easily yielded anatase or rutile on heating).[18]

The Si/Zr oxides arising from alkyl halide elimination remained amorphous after calcination for 5 h at 600 °C.[45] At this stage infrared and ^{29}Si NMR spectroscopy showed a large amount of Si−O−Zr bonds, indicating a homogeneous distribution of the components on an atomic scale. The crystallization of tetragonal zirconia took place at higher temperature; the transformation of tetragonal to monoclinic zirconia was strongly retarded and did not take place after 2 h at 1300 °C. Despite the above-mentioned homogeneity, the crystallization of zircon $ZrSiO_4$ (for a sample containing 50 mol % Zr) did not take place at lower temperature than for conventional xerogels. It only started at 1500 °C, and it was completed after 20 h at 1500 °C. In the same way, no decrease in the crystallization temperature into zircon had been observed for homogeneous nonhydrolytic gels arising from the aprotic condensation between $Zr(OPr^n)_4$ and $Si(OAc)_4$ (Pr^n = n-propyl).[17] This shows that the homogeneity of the precursor gel does not necessarily result in the direct crystallization of the mixed oxide phase.[47]

4.3. Titanates. Recently the preparation of zirconium titanate and aluminum titanate gels by aprotic condensation between metal chloroalkoxides has been reported.[48−50] $ZrTiO_4$ is known as a compound stable at low temperature in the TiO_2-ZrO_2 binary system. Accordingly the direct crystallization of $ZrTiO_4$ below 700 °C, without the intermediate formation of TiO_2 or ZrO_2, was ascribed to the high homogeneity of the nonhydrolytic gels.[49]

However the results observed in the case of aluminum titanate gels are more informative.[50] Actually aluminum titanate is known to be metastable below 1180 °C; where it decomposes into TiO_2 (rutile) and α-Al_2O_3 (corundum). The samples arising from the nonhydrolytic sol−gel way were found to be almost amorphous at 600 °C. At 850 °C, pseudo-brookite β-Al_2TiO_5 was the only crystalline phase present, besides about 10% of amorphous phase. The direct crystallization of metastable aluminum titanate below its temperature range of stability was attributed to the high homogeneity of the gels. Only one similar case had been previously reported by Bonhomme-Coury et al.,[51] with a gel arising from the hydrolysis of a mixture of aluminum *sec*-butoxide and titanium isopropoxide, after the former precursor had been modified with ethyl acetoacetate and the latter with acetic acid. The two results illustrate that homogeneous mixtures may crystallize at low temperature into metastable phases if the low rates of diffusion hinder the phase separation into simple oxides (that is, short-range ordering is preferred to long-range diffusion at low temperatures).[52]

However, in the work of Bonhomme-Coury et al., the gel segregated into thermodynamically stable rutile and corundum at 1230 °C. 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 besides β-Al_2TiO_5. The high stability of aluminum titanate prepared by the nonhydrolytic route was ascribed to the formation of small crystallites, embedded in the amorphous phase, which would be reluctant to grow beyond the critical size in a mechanism of nucleation and growth.

5. Conclusion and Prospects

It is now possible to outline the main features of nonhydrolytic sol−gel processes:

Simple reactions, with easily available compounds, low synthesis temperatures (from room temperature to around 100 °C), and easily removed byproducts (hydrogen halide, alkyl halide, or acetate).

The possibility to use no cosolvent (otherwise needed to get the miscibility of water−alkoxides systems) or, conversely, to combine the advantages of a solvothermal treatment.

The early results presented provide a glimpse of some advantages that may be expected from nonhydrolytic sol−gel processes over the conventional routes.

Low-temperature routes to unhydrated and low-hydroxyl oxides.

An improved control over the molecular level homogeneity and stoichiometry of multicomponent oxides, by circumventing the different reactivity of precursors toward hydrolysis and condensation.

An access to new structures by retaining the complex molecular framework of precursors in solution, otherwise broken by hydrolysis, as in the case of aluminum chloroalkoxides.

Further insights into kinetics are needed to determine the factors governing the mechanisms of nonhydrolytic sol−gel processes that influence the structure and texture of a given metal oxide. Moreover, in our opinion, the nonhydrolytic approach might be developed in the future in the field of hybrid inorganic−organic materials, and as a synthetic route to particular polymetallic oxo clusters. The latter compounds might be used as building blocks in aqueous sol−gel or chemical vapor deposition processes, as indicated by a number of early reports.[10,15,22]

References

(1) Brinker, C. J.; Scherer, G. W. *Sol−Gel Science: The physics and chemistry of sol−gel processing*; Academic Press: San Diego, 1990.
(2) Sanchez, C.; Livage, J.; Henry, M.; Babonneau, F. *J. Non-Cryst. Solids* **1988**, *100*, 65.
(3) Vioux, A.; Leclercq, D. *Heterogeneous Chem. Rev.* **1996**, *3*, 65.
(4) Corriu, R. J. P.; Leclercq, D. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1420.
(5) Shulman, G. P.; Trusty, M.; Vickers, J. H. *J. Org. Chem.* **1963**, *28*, 907.
(6) Acosta, S.; Corriu, R. J. P.; Leclercq, D.; Lefèvre, P.; Mutin, P. H.; Vioux, A. *J. Non-Cryst. Solids* **1994**, *170*, 234.
(7) Bradley, D. C.; Mehrotra, R. C.; Gaul, D. P. *Metal Alkoxides*; Academic Press: New York, 1978.
(8) Gerrard, W.; Woodhead, A. H. *J. Chem. Soc.* **1951**, 519.
(9) Corriu, R. J. P.; Leclercq, D.; Lefèvre, P.; Mutin, P. H.; Vioux, A. *J. Non-Cryst. Solids* **1992**, *146*, 301.
(10) Ridge, D.; Tood, M. *J. Chem. Soc.* **1949**, 2637.
(11) Arnal, P.; Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Vioux, A. *J. Mater. Chem.* **1996**, *6*, 1925.
(12) Goel, S. C.; Chiang, M. Y.; Gibbons, P. C.; Buhro, W. E. *Mater. Res. Soc. Symp. Proc.* **1992**, *271*, 3
(13) Caulton, K. G.; Hubert-Pfalzgraf, L. G. *Chem. Rev.* **1990**, *90*, 969. (b) Hubert-Pfalzgraf, L. G. *Polyhedron* (symposium in press) **1994**, *13*, 1181.
(14) Daniele, S.; Papiernik, R.; Hubert-Pfalzgraf, L. G. *Inorg. Chem.* **1995**, *34*, 628.
(15) Bradley, D. C.; Thomas, I. M. *J. Chem. Soc. A* **1959**, 3404.
(16) Jansen, M.; Guenther, E. *Chem. Mater.* **1995**, *7*, 2110.
(17) Iwasaki, M.; Yasumori, A.; Shibata, S.; Yamane, M. *J. Sol-Gel Sci. Technol.* **1994**, *2*, 387.
(18) Caruso, J.; Hampden-Smith, M. J.; Rheingold, A. L.; Yap, G. *J. Chem. Soc., Chem. Commun.* **1995**, 157.
(19) Caruso, J.; Hampden-Smith, M. J.; Duesler, E. N. *J. Chem. Soc., Chem. Commun.* **1995**, 1041.
(20) Caruso, J.; Roger, C.; Schwertfeger, F.; Hampden-Smith, M. J.; Rheingold, A. L.; Yap, G. *Inorg. Chem.* **1995**, *34*, 449.
(21) Caruso, J.; Hampden-Smith, M. J. *J. Sol−Gel Sci. Technol.* **1997**, *8*, 35.
(22) (a) Sharp, K. G. *J. Sol−Gel Sci. Technol.* **1994**, *2*, 35. (b) In *Hybrid Organic−Inorganic Composites*; Mark, J. E., Lee, C. Y.-C., Bianconi, P. A., Eds.; *ACS Symp. Ser.* **1995**, *585*; Chapter 13.
(23) (a) Corriu, R. J. P.; Leclercq, D.; Lefèvre, P.; Mutin, P. H.; Vioux, A. *J. Mater. Chem.* **1992**, *2*, 673; (b) *Chem. Mater.* **1992**, *4*, 961
(24) Acosta, S.; Arnal, P.; Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Vioux, A. *Mater. Res. Soc. Symp. Proc.* **1994**, *346*, 43.
(25) Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Samson, H.; Vioux, A. *J. Organomet. Chem.* **1994**, *466*, 43.
(26) Yuh, S. K.; Bescher, E. P.; Babonneau, F.; Mackenzie, J. D. *Mater. Res. Soc. Symp. Proc.* **1994**, *346*, 803.
(27) Arnal, P.; Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Vioux, A. *Mater. Res. Soc. Symp. Proc.* **1994**, *346*, 339.
(28) Akhtar, M.; US Patent 5,089,248, 1992.
(29) Arnal, P.; Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Vioux, A. *Chem. Mater.* **1997**, *9*, 694.
(30) Moedritzer K., in Becker, E. I., Tsutsui, M., Eds.; *Organometallic Reactions*; Wiley: New York, 1971; Vol. 2, pp 7−14.
(31) Weingarten, H.; Van Wazer, J. R. *J. Am. Chem. Soc.* **1965**, *87*, 724.
(32) Noll, W. *Chemistry and Technology of Silicones*, 2nd ed.; J. Wiley: New York, 1951.
(33) Andrianov, K. A.; Ganina, T. N.; Sokolov, N. N. *J. Gen. Chem.* **1956**, *26*, 1897.
(34) Turin, E.; Nielson, R. M.; Merbach, A. E. *Inorg. Chim. Acta* **1987**, *134*, 67.
(35) Bachant, B.; Wuest, J. D. *Organometallics* **1991**, *10*, 2015.
(36) Rasuwajew, G. A.; Bobinowa, L. M.; Etlis, V. S. *Tetrahedron* **1959**, *6*, 154.
(37) In general, sol−gel derived solids first crystallize to the phase with the lowest density, which presumably has a structure most resembling that of the glass. Thus titania usually forms anatase (3.90 g/cm^3) at temperatures where rutile (4.27 g/cm^3) is the stable phase (see ref 1, Chapter 12).
(38) Hague, D. C.; Mayo, M. J. *J. Am. Ceram. Soc.* **1994**, *77*, 1957.
(39) Inoue, M.; Kominami, H.; Inui, T. *J. Am. Ceram. Soc.* **1992**, *75*, 2597.
(40) Acosta, S.; Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Vioux, A. *J. Sol-Gel Sci. Technol.* **1994**, *2*, 25.
(41) Yanovskii, A. I.; Kozunov, V. A.; Turova, N. Ya.; Furmanova, N. G.; Stuchkov, Yu. T. *Dokl. Akad. Nauk. SSSR* **1979**, *244*, 119.
(42) (a) Gérardin, C. Sundaresan, S.; Benziger, J.; Navrotsky, A. *Chem. Mater.* **1994**, *6*, 160. (b) Okada, K.; Ban, T.; Yasumori, A. *Eur. J. Solid State Inorg. Chem.* **1995**, *32*, 683.
(43) Acosta, S.; Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Vioux, A. *Mater. Res. Soc. Symp. Proc.* **1994**, *346*, 345.
(44) Heterogeneity leads to the crystallization of a spinel phase at the same temperature. Mullite formed at 980 °C, usually qualified as pseudotetragonal, is aluminium-rich ($Al_2O_3/SiO_2 > {}^3/_2$), with the excess SiO_2 separating as amorphous silica. At higher temperatures the silica and mullite phases react, thus increasing the silicon content in mullite crystals, until the complete transformation into orthorhombique mullite, near 1200 °C. The nonstoichiometry of pseudotetragonal mullite would originate from the fact that, prior to crystallization, homogeneously prepared mullite precursor would phase separate into Al_2O_3-rich and SiO_2-rich amorphous phases, due to the immiscibility gap in the Al_2O_3−SiO_2 system (see ref 42b).

(45) Andrianainarivelo, M.; Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Vioux, A. *J. Mater. Chem.* **1996**, *6*, 1665.

(46) (a) In pure titania gels, this transformation takes place between 600 and 1000 °C. The same suppressive effect on the transformation of anatase to rutile has been reported for some mixed SiO_2-TiO_2 oxides prepared by hydrolytic sol−gel. It was ascribed to the presence of Ti−O−Si bonding at the fringe of fine TiO_2 particles, which prevents the crystal growth and phase transformation of anatase; (b) Nakabayashi, H.; Nishiwaki, K.; Ueno, A. *Mater. Res. Bull.* **1988**, *23*, 555.

(47) An explanation of this behavior could lie in the incongruent melting of zircon, if one keeps in mind the fact that, on heating, sol−gel derived glasses usually follow the same sequence of phase transitions as do melts of the same composition on cooling. In this view the behavior of gels of mullite composition would be an anomaly, even though a phase separation is postulated to occur before crystallization (see ref 44).

(48) Andrianainarivelo, M.; Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Vioux, A. *J. Sol-Gel Sci. Technol.* **1997**, *8*, 89.

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

(50) Andrianainarivelo, M.; Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Vioux, A. *Chem. Mater.* **1997**, *9*, 1098.

(51) Bonhomme-Coury, L.; Lequeux, N.; Mussotte, S.; Boch J. *Sol-Gel Sci. Technol.* **1994**, *2*, 371.

(52) Barboux, P. Griesmar, P.; Ribot, F.; Mazerolles, L. *J. Solid State Chem.* **1995**, *117*, 343.

CM970322A