Communications

Preparation of Monolithic Binary Oxide Gels by a Nonhydrolytic Sol–Gel Process

R. Corriu, D. Leclercq, P. Lefèvre, P. H. Mutin, and A. Vioux*

*UM 44 CNRS/Rhône-Poulenc
Université Montpellier II, case 007
F-34095 Montpellier Cedex 5, France*

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We wish to present here an extension of the non-hydrolytic sol–gel process we described elsewhere for the preparation of monolithic metal oxide gels[1] to the preparation of binary oxide gels. This reaction corresponds to the condensation between metal halides and metal alkoxides (eq 1) under anhydrous conditions.

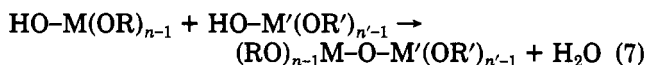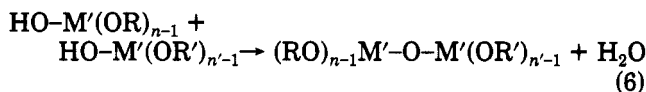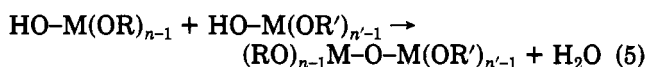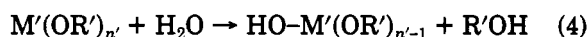$$MX_n + M(OR)_n \rightarrow 2MO_{n/2} + nRX \qquad (1)$$

By using different metals, binary oxide gels may be prepared according to eq 2. Such a cross-condensation

$$mMX_n + nM'(OR)_m \rightarrow M_mM'_nO_{nm} + nmRX \qquad (2)$$

reaction has already been used by Gerrard et al.[2] for the preparation of non-metal oxides, but it has never been reported before with metal components.

The main advantage of the sol–gel route[3] to multicomponent oxides over conventional mixed powder methods resides in the improved homogeneity expected.[4] Indeed molecular precursors (salts or metal alkoxides) are allowed to react in solution at room temperature, thus avoiding phase separation, crystallization, and chemical decomposition. Two types of chemical reaction are involved. First, the hydroxylation of precursors is achieved either by varying the pH in an aqueous solution for salts (nitrates,

chlorides, etc.) or by hydrolyzing metal alkoxides in an organic solvent. Second, the condensation of the hydroxyl groups leads to an oxide network. Equations 3–7 summarize some of the reactions involved during the hydrolysis–condensation of two mixed alkoxides.

$$M(OR)_n + H_2O \rightarrow HO-M(OR)_{n-1} + ROH \qquad (3)$$

$$M'(OR')_{n'} + H_2O \rightarrow HO-M'(OR')_{n'-1} + R'OH \qquad (4)$$

$$HO-M(OR)_{n-1} + HO-M(OR')_{n'-1} \rightarrow$$
$$(RO)_{n-1}M-O-M(OR')_{n'-1} + H_2O \qquad (5)$$

$$HO-M'(OR)_{n-1} +$$
$$HO-M'(OR')_{n'-1} \rightarrow (RO)_{n-1}M'-O-M'(OR')_{n'-1} + H_2O \qquad (6)$$

$$HO-M(OR)_{n-1} + HO-M'(OR')_{n'-1} \rightarrow$$
$$(RO)_{n-1}M-O-M'(OR')_{n'-1} + H_2O \qquad (7)$$

However some difficulties arise with controlling stoichiometry[5] and homogeneity. It appears that the actual homogeneity depends on the relative rate of homocondensation (M–O–M and M'–O–M' bridges) toward heterocondensation (M–O–M' bridges). A possible response is to subject the less reactive alkoxide precursor (e.g., Si(OR)₄) to partial hydrolysis before adding the more reactive one.[6] Another interesting approach is the use of heterometallic alkoxides[7] (yet containing M–O–M' linkage). Nonetheless the reversibility of the reactions in eqs 3–7 (particularly the hydrolysis of M–O–M' bridges) can lead to the formation of the individual components, especially if they are the equilibrium phases.

The nonhydrolytic condensation reaction which leads to the formation of M–O–M' bridges by releasing alkyl halide, as described in eq 8, would imply a perfect alternation of the metal centers M and M'.

$$M(OR)_n + M'X_{n'} \rightarrow (RO)_{n-1}M-O-M'X_{n'-1} + RX \qquad (8)$$
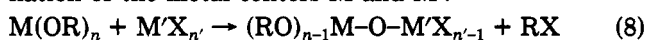
However, rapid ligand-exchange reactions are well-known between metal alkoxides and metal halides:[8]

$$M(OR)_n + M'X_{n'} \rightarrow M(OR)_{n-x}X_x + M'(OR)_xX_{n'-x} \qquad (9)$$
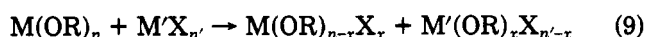
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(2) (a) Gerrard, W.; Griffey, P. F. *Chem. Ind.* **1959**, 55. (b) Gerrard, W.; Jeacocke, G. J. *Ibid.* **1959**, 704. (c) Gerrard, W.; Mooney, E. F.; Rothenbury, R. A. *J. Appl. Chem.* **1962**, *12*, 373.

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Table I. Binary Oxide NHG: Conditions and Time for Gelling, Weight Loss, Oxide Yield, Specific Surface Area Based on the BET Method, and Crystalline Phase after Calcination in Air (i-Pr = Isopropyl; n = Pr = n-Propyl)

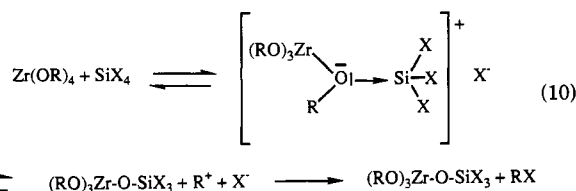| MX_n	SiCl$_4$	$^4/_3$AlCl$_3$	SiCl$_4$	TiCl$_4$	SiCl$_4$	$^4/_3$AlBr$_3$
M(OR)$_n$	$^4/_3$Al(OiPr)$_3$	Si(OiPr)$_4$	Ti(OiPr)$_4$	Si(OiPr)$_4$	Zr(OnPr)$_4$	Ti(OiPr)$_4$
solvent	CCl$_4$(3M)	CCl$_4$/Et$_2$O 0.64 M				CH$_2$Br$_2$ 0.77 M
t_{gel}[b] (T, °C)	2 days (40)	3 days (20)	5 days (40)	15 h (40)	<7 days (110°C)[a]	<7 days (110°C)[a]
$\Delta m/m$,[c] %	54	43	10	22	19	48
yield,[d] %	100	84	100	100	99	75
surface,[e] m^2/g (T, °C)	364 (750)	160 (600)	590 (500)		386 (600)	255 (650)
X-ray[e]	amorphous	amorphous	anatase		amorphous	anatase[f]

[a] In sealed tube. [b] Time at which no flow of the gel was observed by tipping the container. [c] Measured by thermal gravimetric analysis to 1200 °C. [d] Final yield based on the theoretical oxide formula. [e] Determined after oxidation of the residual organic groups (5-h heat treatment at the temperature given in parentheses). [f] Broad lines.

Therefore homogeneity depends on the relative rates of condensation of the halogenoalkoxides formed. However the process appears simpler to control than the conventional hydrolysis–condensation double process. Homogeneity, that is, the quasi-random mixture of bonding M–O–M, M'–O–M' and M–O–M', will be achieved in the nonhydrolytic gel (NHG) if all the condensation rates are of the same order.

This work deals with the preparation of oxide gels in the bicomponent systems Si–Al, Si–Ti, Si–Zr, and Al–Ti by mixing metal halides with metal alkoxides. Reactions were carried out in solution when one component (the halide or the alkoxide) was solid, and without solvent when the two components were liquid. The molar ratio of components was based on the stoichiometry of the reaction (eq 2). Monolithic gels (i.e., gels extending throughout the initial volume of the liquid) were obtained, at room temperature or by heating in sealed vials (Table I).

In the binary system Si–Al the gel time did not depend on the metal precursor (aluminum alkoxide or aluminum halide). Conversely in the system Si–Ti the gel time was shorter for the couple titanium chloride–tetraisopropoxysilane than for the system titanium isopropoxide–tetrachlorosilane (which is not consistent with a complete redistribution of the ligands around Si and Ti atoms before condensation reactions).

The liquid expelled from the gel by spontaneous shrinkage (syneresis process) was analyzed by ^{1}H NMR and gas chromatography (GC). No alcohol related to hydrolysis was detected; the only byproduct was alkyl halide. Thus, gelation originated from the nonhydrolytic condensation reaction. It is noteworthy that a significant amount (around 75%) of isopropyl halide was identified besides the expected n-propyl halide in the case of SiCl$_4$-Zr(OnPr)$_4$ system. This is consistent with the intermediate formation of a carbocation (typical of a first-order nucleophilic substitution S_N^1, eq 10) which partly rearranges into the more stable secondary (isopropyl) carbocation.

$$Zr(OR)_4 + SiX_4 \rightleftharpoons \left[(RO)_3Zr \underset{R}{\overset{}{\diagdown}} \ddot{O}| \longrightarrow Si \begin{matrix} X \\ X \\ X \end{matrix} \right]^+ X^- \quad (10)$$

$$\rightleftharpoons (RO)_3Zr\text{-O-}SiX_3 + R^+ + X^- \longrightarrow (RO)_3Zr\text{-O-}SiX_3 + RX$$

The overall yields in binary oxide were determined after calcination in air and appeared satisfactory (from 75 to

Table II. Compositions of the Binary Oxide NHG.

$MX_n/$ $M'(OR)_n$	T °C	%M	%M'	%X	%C	%H	M/M' ratio
		elem anal.					
$^4/_3$AlCl$_3/$ Si(OiPr)$_4$	550	22.95	18.01	0.15	0.43	1.14	Al/Si = 1.32
SiCl$_4/$ Ti(OiPr)$_4$	500	18.70	31.35	0.58	0.46	0.56	Si/Ti = 0.98
$^4/_3$AlBr$_3/$ Ti(OiPr)$_4$	600	22.40	29.94	0.20	0.17	0.47	Al/Ti = 1.33

100%). X-ray diffraction (Table I) indicated the formation of crystallites of anatase TiO$_2$ in Si–Ti (Figure 1a) and Al–Ti systems, after calcination in the range 500–700 °C. Table II displays the elemental analysis of some of the gels after calcination at the mentioned temperature. The binary oxides are practically carbon-free. The metal content of the binary oxides is very close to the composition of the starting solution (as expected from the yields found). The microchemical analytical study of the Si–Ti sample in Table II (and of the Si–Zr sample in Table I) by means of an electron-probe microanalyzer[10] indicated a constant Ti/Si (Zr/Si) ratio (close to 1, based on 10-point measurements) which is consistent with homogeneity at the micrometer level.

Homogeneity on an atomic scale would lead to bicomponent oxide (if it exists) on crystallization, instead of mixtures of single oxide.[4] However the compositions of our Si–Al and Ti–Al systems (Table II) are far from the compositions of mullite (3Al$_2$O$_3$, 2SiO$_2$) and aluminum titanate (Al$_2$O$_3$, TiO$_2$), respectively. The nonformation of zircon ZrSiO$_4$ (TiSiO$_4$ does not exist) as the first crystalline phase in the Zr–Si system in the 50/50% composition has been previously discussed.[9] It is interesting to note that our sample just started to crystallize (tetragonal ZrO$_2$) at 1000 °C (Figure 1b).

^{29}Si solid-state MAS (magic angle spinning) NMR spectrometry gives more direct information on the extent of M–O–M' bonding. The spectra of Si–Ti and Si–Zr NHG (Figure 2) indicated a large chemical shift distribution centered at –102 ppm. The spectra were similar to those obtained for particular hydrolytic gels TiO$_2$/SiO$_2$[11] in which the presence of Si–O–Ti bonding was inferred from the large contribution of Q^2 sites (two next-adjacent Ti atoms) and Q^3 sites (one next-adjacent Ti atom), near –91 and –102 ppm, respectively. Compositions with smaller Ti (or Zr) content are currently investigated as being less favorable to phase separation.[12,13]

In conclusion the nonhydrolytic sol–gel method described here appears simple and general to prepare mon-

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(10) Energy-dispersive spectroscopy, 25-kV acceleration potential, 33.0° takeoff angle, 7.5-mm-thick Be window.

(11) Gels prepared by addition of the titanium alkoxide at a stage where the silicon alkoxide hydrolysis has only proceeded to about 50%, on average. Walther, K. L.; Wokaun, A.; Handy, B. E.; Baiker, A. *J. Non-Cryst. Solids* **1991**, *134*, 47.

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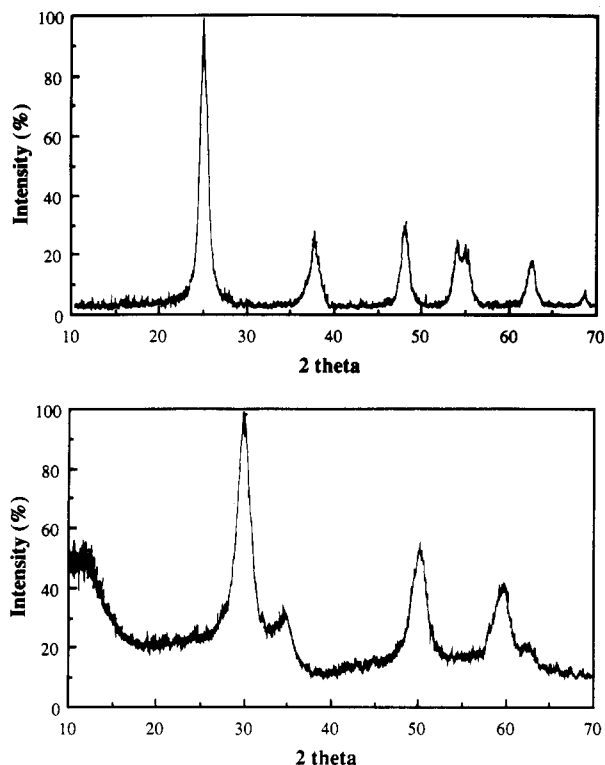
Figure 1. X-ray diffraction patterns for calcined NHG: (a, top) anatase (NHG prepared from $SiCl_4$-$Ti(OiPr)_4$ system then calcined at 500 °C for 5 h in air); (b, bottom) tetragonal zirconia (NHG prepared from $SiCl_4$-$Zr(OnPr)_4$ system then calcined at 1000 °C for 5 h in air).
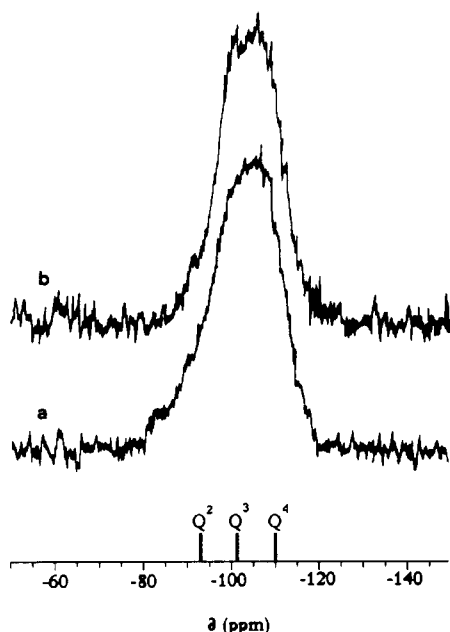
Figure 2. ^{29}Si solid-state MAS NMR spectra (on a BRUKER AM 300 apparatus, 30° flip angle, 20-s recycle delay time, chemical shifts referenced to TMS) for calcined NHG: (a) SiO_2-ZrO_2 (NHG prepared from $SiCl_4$-$Zr(OnPr)_4$ system then calcined at 600 °C); (b) SiO_2-TiO_2 (NHG prepared from $SiCl_4$-$Ti(OiPr)_4$ system then calcined at 500 °C).

olithic gels either in silica-based or in mixed-metal oxides; it allows controlling the composition of binary oxides. Further investigations are in progress to improve the comparison of NHG with conventional hydrolytic gels.

Poled, Chromophore-Functionalized Polymeric Nonlinear Optical Materials. Probing Second Harmonic Generation Temporal Characteristics via Site-Selective Cross-Linking/Hydrogen Bonding

Yi Jin, Stephen H. Carr, and Tobin J. Marks*

Departments of Chemistry
Materials Science and Engineering
and the Materials Research Center
Northwestern University
Evanston, Illinois 60208-3113

Weiping Lin and George K. Wong*

Department of Physics and Astronomy and
the Materials Research Center
Northwestern University, Evanston, Illinois
60208-3113

Appending high-β chromophores to glassy macromolecules represents an advance in NLO materials[1] design in that chromophore number densities are greatly enhanced and structural disorientation/physical aging processes subsequent to cessation of electric field poling are impeded.[2,3] Further enhancements in the SHG (second harmonic generation) temporal stability of such materials can be achieved by effecting thermal cross-linking/vitrification of the matrix in concert with the poling process.[2a,4,5] Nevertheless, optimum architectural strategies for such cross-linking processes, either chemical or hydrogen hydrogen-bonding, have not been systematically addressed. We report here modifications of our previously investigated

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