

Novel Non-Hydrolytic Sol-Gel Route to Metal Oxides

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Abstract. Monolithic alumina and aluminosilicate gels have been prepared using a novel sol-gel process based on the non-hydrolytic condensation reaction between a metal halide and a metal alkoxide. XRD indicated that the alumina gel remained amorphous at 750°C; solid state ^{27}Al NMR indicated the presence in the dried gel and in the amorphous calcined sample of a large amount of pentacoordinated aluminum atoms. A study of the sol formation using liquid state ^{27}Al NMR suggested that the gel structure was reminiscent of the oligomeric structure of the chloroisopropoxide precursors. Differential thermal analysis and XRD indicated that the aluminosilicate gels were converted to mullite below 1000°C, suggesting a high degree of homogeneity in these precursors.

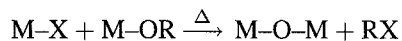
Keywords: non-hydrolytic gelation, gelation mechanism, alumina gel, mullite, chloroalkoxides

1. Introduction

Much work has been directed towards the synthesis of metal oxides and complex metal oxides by sol-gel processing of metal alkoxides, based on the hydrolysis and polycondensation reactions. In this paper we would like to give a brief survey of the possibilities offered in this field by another sol-gel route, based on *non-hydrolytic* reactions.

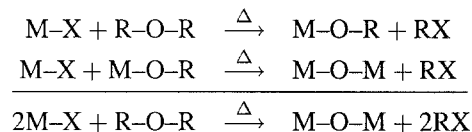
2. Background

In conventional sol-gel processes, sol and gel formation is due to the formation of M-O-M bridges through hydrolysis and polycondensation reactions. Any reaction leading to the same bridges in good yields could afford an alternative sol-gel route. Thus, in the non-hydrolytic sol-gel process we are developing, [1] M-O-M bridges result from the condensation between metal halides (typically chlorides) and metal alkoxides (typically isopropoxides), with elimination of alkyl halide:

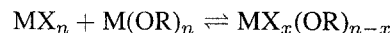


We also use a related reaction, namely the etherolysis of metal halides by organic ethers, [2] such as diisopropylether or THF, which leads to the intermediate

formation of chloroalkoxides:



Although no systematic study has been made of the mechanism of these reactions, they are very likely initiated by the coordination to the metal of the oxygen of the alkoxide (or the ether), [2] followed by the nucleophilic substitution of the R group by the halide anion. In most cases these reactions are thermally activated and, depending on the reactives involved, temperatures ranging from room temperature to about 100°C are required. Actually, when a metal halide and a metal alkoxide are mixed together, the first reaction that takes place is a rapid exchange of the ligands, leading to a mixture of halogenoalkoxides, [3] which are thus the *true precursors* in our non-hydrolytic sol-gel process:



3. Applications

A variety of oxides and binary oxides of Si, Al, Ti or Zr has already been prepared by this route. [1] In this communication, we wish to report the examples of Al_2O_3

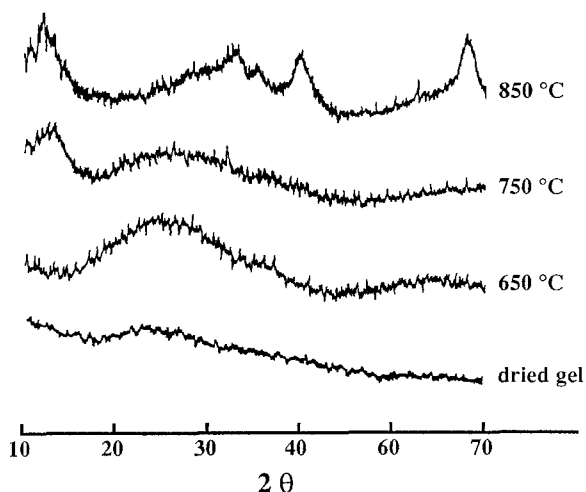
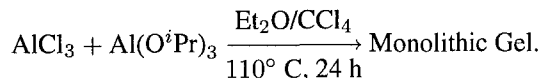


Fig. 1. XRD pattern of dried Al_2O_3 gel, calcinated at 650°C for 5 hours, and annealed at 750°C and 850°C for additional hours.

and mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) in order to illustrate some of the originalities of this sol-gel route.

3.1. Preparation of Amorphous Alumina With High Al^{V} Content

Non-hydrolytic alumina gels have been prepared using AlCl_3 and $\text{Al}(\text{O}^i\text{Pr})_3$ (in stoichiometric amounts) as precursors:



Structural investigation of the dried gel and the alumina obtained by calcination was performed by means of X-ray diffraction (XRD) and ^{27}Al magic angle spinning nuclear magnetic resonance (MAS/NMR). These studies revealed significant differences in comparison with processes based on the hydrolysis of alkoxides.

The gels prepared from AlCl_3 and $\text{Al}(\text{O}^i\text{Pr})_3$ precursors are amorphous according to XRD (Fig. 1). Moreover, they remain amorphous after calcination for 5 hours at 750°C; crystallization (as $\gamma\text{-Al}_2\text{O}_3$) occurs after 5 hours at 850°C. As a comparison, hydrated alumina gels obtained by hydrolysis of alkoxide precursors or boehmite usually crystallize to $\gamma\text{-Al}_2\text{O}_3$ at 400–500°C. [4]

The aluminum atoms in aluminas are in most cases tetraordinated (Al^{IV}) or hexacoordinated (Al^{VI}). [5] However, pentacoordinated Al atoms (Al^{V}) have been evidenced by ^{27}Al NMR in a very few cases. Indeed,

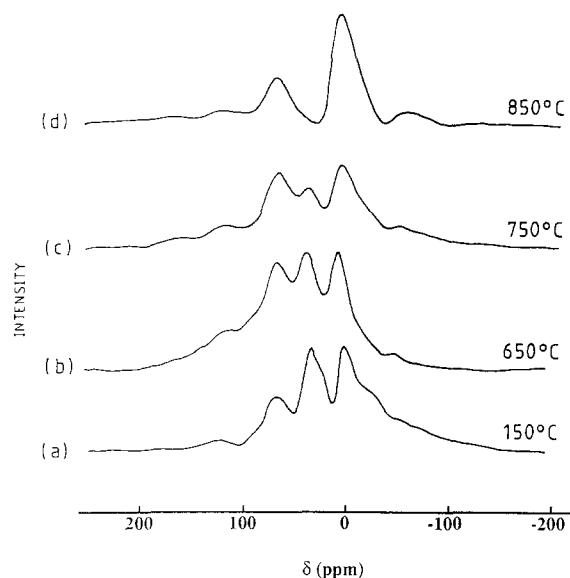
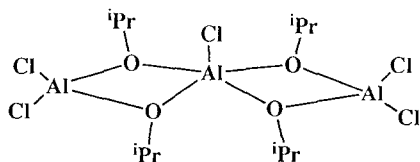


Fig. 2. ^{27}Al MAS-NMR spectra of dried Al_2O_3 gel, calcinated at 650°C for 5 hours, and annealed at 750°C and 850°C for additional hours.

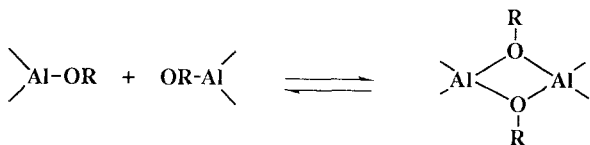
the chemical shift of ^{27}Al nuclei in aluminas is very sensitive to the coordination number with oxygen: the resonance of Al^{IV} sites is between 55 and 70 ppm, that of Al^{V} is observed between 25 to 35 ppm and that of Al^{VI} between 0 and 11 ppm. Thus, significant amounts of Al^{V} sites were detected in a ρ -alumina obtained by calcining gibbsite at 200°C *in vacuo*. [5a] These sites were also observed in transition aluminas derived either from finely divided gibbsite and boehmite, [6] or from alumina gels prepared by the *in-situ* generation of a base. [7] In our case, the intense peak at *ca* 35 ppm in the ^{27}Al MAS-NMR spectrum of the xerogel shows that Al^{V} sites are already present in this sample. In addition, these sites are retained in the calcined samples up to the crystallization, above 750°C (Figure 2).

These pentacoordinated Al sites could have different origins: they could be formed during the gelation or the drying of the gel or they could be related to the structure of the aluminum chloroisopropoxides. Indeed, chloroisopropoxides of aluminum were reported to exist as trimers either in solution or in the solid state. For instance, $\text{Al}_3\text{Cl}_5(\text{OPr}^i)_4$, has a linear trimeric structure [8] with one pentacoordinated Al atom in the center and two tetraordinated Al atoms on the ends as shown in scheme 1.

To check this latter hypothesis, we have followed by ^{27}Al NMR the structural changes occurring during the sol formation (Fig. 3). The spectrum of the start-



Scheme 1



Scheme 2

ing $\text{AlCl}_3/\text{Al}(\text{O}^i\text{Pr})_3$ solution before heating shows a peak at 100 ppm with a shoulder at 91 ppm, ascribable to tetracoordinated Al atoms bonded to both Cl and ^iPr groups. A large peak is observed at 45 ppm; this value is intermediate between that observed for Al^{V} sites in trimeric $\text{Al}(\text{O}^i\text{Pr})_3$ (33.1 ppm) [9] and $\text{AlCl}_3 \cdot 2\text{THF}$ (63 ppm), [10] and is consistent with the chemical shift expected for the pentacoordinated Al atom bonded to 1 Cl atom and 4 oxygen atoms in the trimeric structure showed in scheme 1. Integration indicates that these two peaks are in a 2:1 ratio, which is consistent with a predominantly trimeric structure. [9] When the solution is heated at 110°C for 12 and 18 hours (gel time $\cong 24$ hours) (Fig. 3), condensation occurs, leading to the appearance of a new peak at ca 70 ppm, indicating the presence of tetracoordinated Al bonded to four O atoms. [5] Interestingly enough, the Al^{V} sites are retained during the sol formation. This behavior strongly suggests that the Al^{V} sites observed in the dried gel originate from the Al^{V} sites of the trimeric chloroisopropoxide precursors which are retained during the gelation and drying process. This result is at the opposite of that observed in the hydrolytic alumina sols. [11] The stability of the oligomeric structure during dehalogenoalkylation is likely related to the mechanism of this reaction. Indeed, the association in halogenoalkoxides and alkoxides arises from the formation of alkoxo bridges. Whereas the hydrolysis reaction involves the cleavage of M–O bonds, and thus of alkoxo bridges, the dehalogenoalkylation involves the cleavage of O–C bonds. Consequently, the formation of the oxide network does not require the cleavage of the oligomer skeleton, as illustrated in scheme 2.

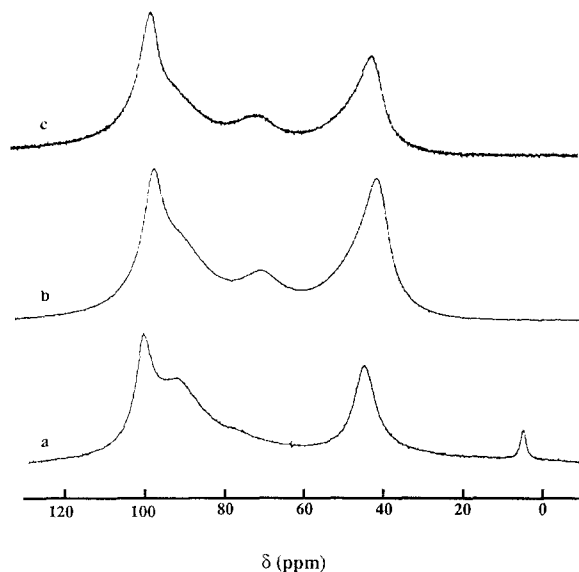
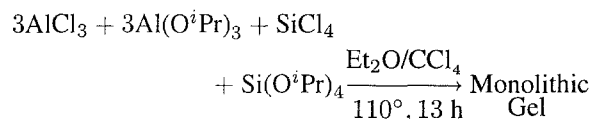


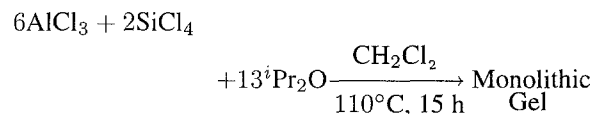
Fig. 3. ^{27}Al MAS-NMR spectra of the starting $\text{AlCl}_3/\text{Al}(\text{O}^i\text{Pr})_3$ solution (a), isothermally heat treated in sealed tubes at 110°C for 12 hours (b) and 18 hours (c).

3.2. Preparation of an Aluminosilicate Gel, Precursor to Mullite

The non-hydrolytic sol-gel process appears well suited to the preparation of binary oxides. Indeed, any composition is theoretically attainable, provided that the number of halide groups (X) is equal to the number of alkyl groups (R) (in the alkoxides $\text{M}(\text{OR})_n$ or in the ether R_2O). In the following, we wish to compare the conversion to mullite, $\text{Al}_6\text{Si}_2\text{O}_{13}$, of two gels with the same composition ($\text{Al}/\text{Si} = 3$) but obtained in two different ways. The first gel (gel I) is obtained from alkoxide and chloride precursors:



The second sample (gel II) is prepared by etherolysis of chlorides:



The monolithic brown gels obtained were dried at 110°C *in vacuo* and their conversion to mullite was followed using differential thermal analysis (DTA) and XRD. In the range 600°C to 1400°C , the DTA curves

exhibited a single sharp exothermic peak at 985°C in both cases; the exothermic peak at 1200°C, which is usually associated with inhomogeneous gels, was not detected. XRD spectra of the gels calcined at 1000°C were characteristic of well crystallized mullite. According to B.E. Yoldas, [12] the spontaneous crystallization of mullite at $\cong 980^\circ\text{C}$ is indicative of a high degree of homogeneity and of the presence of a polymerized aluminum-silicon network. Thus, both etherolysis of chlorides and condensation of alkoxides with chlorides lead to homogeneous gels.

4. Conclusions

The non hydrolytic sol-gel process affords an interesting and easy alternative route to metal and transition metals oxides and more particularly multicomponent oxides. Indeed, the first results obtained indicate that the gels obtained by the reaction of chlorides with either alkoxides or with ether precursors are quite homogeneous. The mechanisms of sol and gel formation appears completely different of the ones involved in hydrolytic methods; in particular, the structure of the oligomeric chloroalkoxide precursor appears to be preserved during the whole process (at least in the case of aluminum) which offers many exciting possibilities such as the control of the coordination state of the metal in the final material.

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