Synthesis of SiO$_2$-TiO$_2$ Xerogels by Sol-Gel Process

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Abstract. A new method to synthesize SiO$_2$-TiO$_2$ gels by sol-gel process has been developed. This technique uses tetraisopropylorthotitanate [Ti(Oipr)$_4$] and tetraethylorthosilicate [TEOS]: they are mixed in the same solvent and then directly hydrolysed. This one-step reaction is possible because of the use of 2-methoxyethanol, a protic polar solvent. This alcohol plays two different specific roles: it acts as a solvent as well as a stabilizer of titanium alkoxide towards the hydrolysis-precipitation reaction. So, by an accurate adjustment of the quantity of methoxyethanol in the mixture, we can control the reactivity of the titanium precursor.

Monolithic and transparent xerogels were obtained whatever the composition. Three monolithic SiO$_2$-TiO$_2$ gels containing 20, 50 and 75 mol% of TiO$_2$ were prepared and studied in details.

By using the TG-DSC analysis, we can follow the evolution of the loss of water and organic residues.

The structural evolution of gels during calcination is characterized by IR spectroscopy and X-Ray diffraction.

Keywords: SiO$_2$-TiO$_2$ glasses synthesis, gelation time, I.R. analysis, crystallization, textural properties

1 Introduction

The SiO$_2$-TiO$_2$ glasses show remarkable properties in fundamental research as well as in industrial applications. As a matter of fact, they have a very small thermal expansion coefficient [1] and a high refractive index [2]. These two properties allow to use the SiO$_2$-TiO$_2$ glasses in the fabrication of pieces in aerospace (optical blooming coating and reflecting telescopes [3]). Unfortunately, these glasses are very difficult to produce by the classical process which involves the fusion of silica and titania oxides. Indeed, this process requires temperatures greater than 1550°C [4] and is only possible in a narrow Ti/Si ratio (when the TiO$_2$ content becomes too high, isolated phases appear in the mixing and devitrification occurs by crystal formation during the cooling).

These difficulties can be overcome by the sol-gel process which allows to obtain high temperature materials with high purity and homogeneity by working at relatively low temperatures. Nevertheless, the major difficulty in this synthesis consists in ensuring a good molecular homogeneity. So it is necessary to develop a statistical repartition of Si and Ti atoms from the starting reactional mixing, hoping that this repartition will always be conserved in the gel dried and then calcined. Such a homogeneity in the multicomponent gels requires nearly equal hydrolysis and condensation reaction rates of both reactive species [5]. However, it is well known that the reactivities of titanium and silicon alkoxides towards hydrolysis are different [6].

With such constraints, several experimental procedures of SiO$_2$-TiO$_2$ glasses synthesis by sol-gel process are developed in the literature. They are based either on a complexation of the titanium precursor, or on a previous partial hydrolysis of the silicon precursor:

- reaction between colloidal silicon and a stable soluble titanium component [7];
- reaction between a titanium alkoxide and a silicon alkoxide first hydrolysed [8];
- reaction between silicic acid and a titanium chelate [9];
- mixing of alkoxides followed by hydrolysis [10].

These methods show a few disadvantages: they are not very convenient and require sometimes very long gelation times. Moreover, they do not necessarily produce homogeneous and transparent gels.
In this work, a new method to synthesize SiO$_2$-TiO$_2$ gels has been studied using methoxyethanol both as solvent and stabilizer of titanium isopropoxide. The interest in using methoxyethanol for the synthesis based on titanium alkoxide was first shown by Budd [11]; moreover, this solvent was also already used in our laboratories for previous sol-gel studies, for example for the synthesis of zirconium oxide-yttrium oxide gels [12]. A complete description of the synthesis and the calcination processes of gels in order to obtain SiO$_2$-TiO$_2$ glasses is given in this paper.

2 Experimental Procedure

2.1 Sample Preparation

Variable quantities of TEOS are added to a titanium isopropoxide solution in methoxyethanol (molar ratio = 0.5). After mixing, a methoxyethanol/water solution is added dropwise to the solution under vigorous stirring (the water used for hydrolysis was first acidified down to pH = 1 by addition of HCl 12N and then diluted in methoxyethanol).

The methoxyethanol repartition in the hydrolysis solution permits to lower the water content locally; consequently, the formation of TiO$_2$.2H$_2$O colloids (white cloudiness) is hindered. The vigorous stirring prevents local concentration gradients.

HCl also plays an important role in this synthesis not only as catalyst but especially as antifloculent agent. As a matter of fact, other acids like HNO$_3$, H$_2$SO$_4$, CH$_3$COOH were tested and lead to the formation of a white precipitate.

From all our experiments, we concluded that a pH ≤ 1 is necessary to obtain homogeneous and transparent gels.

31 mixed Si/Ti gels of different compositions were synthesized (Table 1).

These experiments showed that:

- it is possible to produce homogeneous and transparent gels when the hydrolysis ratio $H$ (defined by the molar ratio between water and metallic precursors [H$_2$O]/[Ti(O'Pr)$_4$] + [TEOS]) ranges from 1.2 to 2. For hydrolysis ratios $H > 2$, two phenomenons are observed:
  - either, the solution gels before the total addition of the solution alcohol-water-HCl;
  - or a flocculation takes place, giving an opaque gel whatever the HCl concentration.

For hydrolysis ratios $H < 1.2$, no gelation is observed.

- the gelation times at room temperature (defined as the time at the end of which the gel has lost its fluidity) are very short: they range from a few minutes to about 1 h 30.
- the methoxyethanol allows the preparation of silicatitania gels in the full composition range for very short gelation times. Moreover, under particular aging and drying conditions, it is possible to produce monolithic gels.

- an exponential decrease of the gelation time as a function of the hydrolysis ratio $H$ is observed (Fig. 1). The smaller the quantity of methoxyethanol MA in the mixture A (which causes a decrease of the stabilizing effect on titanium), the shorter the