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Influence of the synthesis route on sol–gel SiO_2–TiO_2 (1:1) xerogels and powders

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Abstract

Five different sol–gel routes are used in order to synthesize mixed SiO_2–TiO_2 materials. Simple mixing of the Ti and Si precursors, pre-hydrolyzing of TEOS, modification of the Ti alkoxide with acetic acid, isoamyl alcohol and acetylacetone lead to translucent gels with different time of gelation. Different techniques such as TGA, DTA, XRD and IR spectroscopy are used to characterize each material. IR spectroscopy revealed the presence of Si–O–Ti and Si–O–Si bonds for all the xerogels letting suppose a composite microstructure of the gels. Pre-hydrolyzing of TEOS and modification of Ti alkoxide with isoamyl alcohol are the most appropriate routes to retain the anatase phase up to 1100 °C.

Keywords: Sol–gel; Oxide; Microstructure

1. Introduction

Sol–gel process has became one of the most popular routes to synthesize mixed oxides materials as various as SiO_2–TiO_2 [1–4], SiO_2–ZrO_2 [5], Ag_2O–SiO_2 [6], WO_3–ZrO_2 [7] and WO_3–TiO_2 [8]. Among all these systems SiO_2–TiO_2 has received much attention due to its possible application in catalysis [9–11] and optic [12–14]. A great diversity of materials could be obtained by changing the composition of the primary sol and/or the thermal treatment. The nature of the precursor, the molar ratio between the silicon and the titanium alkoxide, the nature of the solvent, the use of modifying agents influence the microstructure and thus the properties of the resulting material.

Tetraethoxysilane (TEOS), titanium isopropoxide (TIP) and ethanol (EtOH) are largely employed to produce mixed titania–silica materials. The main difficulty that has to be overcome, to success in the preparation of materials where titanium and silicon are mixed in the atomic or molecular level, is the difference of reactivity of TEOS and TIP towards hydrolysis and condensation reactions.

TIP is known as very sensitive to hydrolysis due in part to its monomeric form in organic solution [15] leading to a rapid precipitation of a polydisperse product [16]. In order to decrease the reactivity of TIP it is possible to modify this precursor using acetic acid or acetylacetone. On the other hand, TEOS is known to be less sensitive to hydrolysis than transition metal alkoxides, indeed Si is less electropositive and is has no coordination undersaturation [16] in $Si(OEt)_4$. Thus, in the case of silicon alkoxides, acid or basic catalysts have to be used to enhance the hydrolysis and condensation reactions.

The aim of this work is to study and compare different sol preparations in view to obtain homogeneous xerogels (without demixion) in the 1:1 SiO_2–TiO_2 system.

2. Experimental

2.1. Products and characterization techniques employed

TIP (Strem Chemicals), TEOS (Strem Chemicals), EtOH (Merck), acetylacetone (Merck), isoamyl alcohol (Merck), acetic acid (Prolabo) are employed for the different preparations.

Viscosity is studied on a CARRI-MED CSL 100 rheometer.

Thermal analyses (DTA-TGA) are carried out on a SETARAM TG-DTA 92 equipment in the range 30–1200 °C, 70 mg of the xerogel dried at room temperature during 24 h is used in each run and the heating rate is fixed at 10 °C/min.

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Thermo-mechanical analyses are realized using a SETARAM TMA 92 equipment, dried gels are densified under 2.5 MPa, the pellets thus obtained are 5 mm in diameter and 0.5 mn in thickness, the applied load during the analyses is fixed at 20 g and the heating rate at 10 °C/min.

X-rays diffraction data are collected using a PHILIPS X'Pert MPD diffractometer in the $\theta/2\theta$ mode for the powder samples. Cu Kα wavelength is used, the scan conditions are 0.04° 2θ for the step, 4 s for the time per step and 20–80° 2θ for the range over which the diffraction patterns are recorded. The crystallite size is evaluated from the Scherrer relation:

$$t = \frac{0.9.\lambda}{\mathrm{FWHM}\cos(\theta)}$$

where t is the crystallite size, FWHM the full width at half maximum (corrected from a Si standard sample) of the diffraction peak and θ is the angle of incidence. The value of t is averaged over all the diffraction peaks.

The infrared spectra are recorded on a FTIR NICOLET-210 spectrometer on the range 40–1400 cm^{-1} using the KBr pellet technique.

For the XRD and IR analyses with the temperature the samples were heated during 3 h at the desired temperature and the heating rate is fixed at 5 °C/min.

2.2. Preliminary sets of experiments

In a first approach of the system TEOS/TIP/EtOH/HOAc/H_2O we study the effect of the alkoxides concentration on the time of gelation (t_g). 0.015 mol of TEOS and TIP are introduced in 7.19 ml of EtOH under stirring, the solution is then hydrolyzed by a mixture of H_2O/HOAc/EtOH with the molar ratio of hydrolysis ($h = [H_2O]/[TEOS]$) fixed at 4.5, the molar ratio [HOAc]/[TIP] fixed at 1/3 and the volume of EtOH corresponding to the desired concentration. We note that no mineral acid is added to the water for the hydrolysis of TEOS. Fig. 1 shows the evolution of t_g (defined as the time at the end of which the sol has lost its fluidity) as a function of the alkoxides (TIP and TEOS) concentration. We observe, for a fixed ratio of hydrolysis, that a range of concentration allows the formation of translucent gels. Below a concentration of 0.5 mol/l the sol becomes stable and above a concentration of 1.1 mol/l the formation of the gel is instantaneous or the system precipitates. In Table 1 are given the quantities (ml) of all the products used in this study.

Table 1
Quantities (ml) of the products used for the investigation of the alkoxides concentration

	c (mol/l)						
	0.5	0.6	0.7	0.8	0.9	1.0	1.1
TIP	4.46	4.46	4.46	4.46	4.46	4.46	4.46
TEOS	3.35	3.35	3.35	3.35	3.35	3.35	3.35
H_2O	1.215	1.215	1.215	1.215	1.215	1.215	1.215
HOAc	0.286	0.286	0.286	0.286	0.286	0.286	0.286
ETOH	50.69	40.69	33.54	28.19	24.02	20.69	17.96

The second parameter under investigation is the molar ratio of hydrolysis. The same experimental procedure as the preceding one is adopted here. As it can be seen in Fig. 2 this parameter influences the time of gelation for a fixed concentration of TIP and TEOS (1.5 mol/l) and a fixed water to acetic acid ratio ($[H_2O]/[HOAc] = 13$). The range over which the formation of a translucent gel is observed spreads from 0.5 up to 4.5. In Table 2 are given the quantities (ml) of all the products used in this study.

We finally study, in this first approach, the influence of the reflux (80 °C/4 h) on a 1:1 mixture of 0.015 mol of TIP and TEOS in ethanol (7.19 ml). After cooling, the hydrolysis of the system is obtained by adding a HNO_3 (53 wt%) solution, thus the final pH of the solution is less than 1. Fig. 3 presents the results concerning the influence of the molar ratio of hydrolysis on the time of gelation for the preparations with and without reflux. The reflux decreases the time of gelation, this effect is more pronounced for the low molar ratio of hydrolysis. During

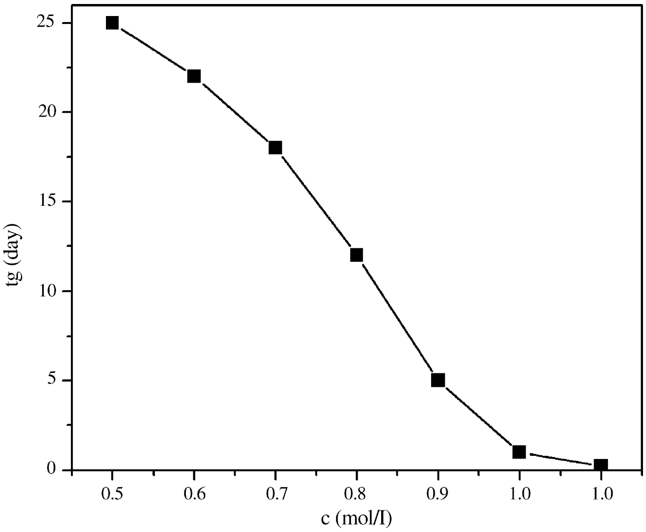

Fig. 1. Influence of the alkoxides (TEOS + TIP) concentration on the time of gelation (t_g).

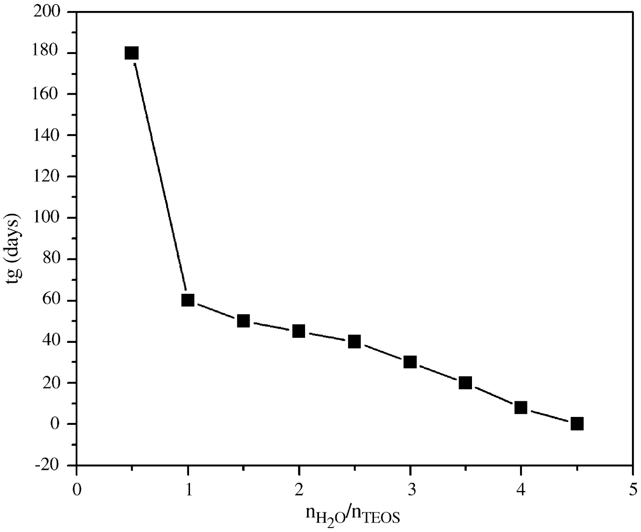

Fig. 2. Influence of the molar ratio of hydrolysis on the time of gelation.

Table 2
Quantities (ml) of the products used for the investigation of the molar ratio of hydrolysis

	$[H_2O]/[TEOS]$								
	0.5	1	1.5	2	2.5	3	3.5	4	4.5
TIP	4.46	4.46	4.46	4.46	4.46	4.46	4.46	4.46	4.46
TEOS	3.35	3.35	3.35	3.35	3.35	3.35	3.35	3.35	3.35
H_2O	0.135	0.27	0.405	0.54	0.675	0.81	0.945	1.08	1.215
HOAc	0.033	0.066	0.099	0.132	0.165	0.198	0.231	0.264	0.296
EtOH	12.02	11.85	11.686	11.518	11.35	11.182	11.014	10.846	10.679

Table 3
Quantities (ml) of the products used for the investigation of the reflux

	$[H_2O]/[TEOS]$				
	3	4	5	6	7
TIP	4.46	4.46	4.46	4.46	4.46
TEOS	3.35	3.35	3.35	3.35	3.35
HNO_3	1.3	1.74	2.17	2.61	3.04
EtOH	10.9	10.45	10.01	9.58	9.15

this step, alcoholic exchange is possible between isopropoxy groups arising from the titanium alkoxide and ethoxy groups arising from the silicon alkoxide and the solvent. Moreover, the comparison of Figs. 2 and 3 illustrates the importance of the pH on the evolution of the sol. Indeed, for $h = 4$, the time of gelation is 8 days when the hydrolysis is generated toward the addition of H_2O/EtOH/HOAc solution and more than 30 days for a concentrated nitric acid solution. For the first case, pH is more than 2.5 and can be viewed as a basic catalyst preparation considering the sole silicon alkoxide and for the second case pH being less than 2.5 the preparation can be viewed as an acid catalyst. The other difference between these two preparations is the ability of acetate ions to modify the titanium alkoxide. In Table 3 are given the quantities (ml) of all the products used in this study.

2.3. Preparation of five different sols

The preliminary set of experiments leads to the preparation of sols following five routes. In order to compare these preparations the concentration of alkoxides (TIP + TEOS) is fixed at 1.5 M in ethanol.

The first preparation consists in realizing a simultaneous hydrolysis of the both alkoxides. We thus mix 0.015 mol of TIP and TEOS in 7.19 ml of ethanol under reflux (80 °C) and under stirring during 8 h, after cooling we add 5 ml of EtOH and let the solution be hydrolyzed by air moisture. The reflux participates to the homogenization of the mixture, it can enhance the electronic interactions between the precursors leading to the possible creation of some Si–O–Ti chemical bonds and alcoholic exchange reactions can modify the reactivity of both alkoxides. We note this first preparation "sol A". This route presents two main disadvantages, firstly it is not possible to control the water content introduced in the sol and secondly the solvent evaporates.

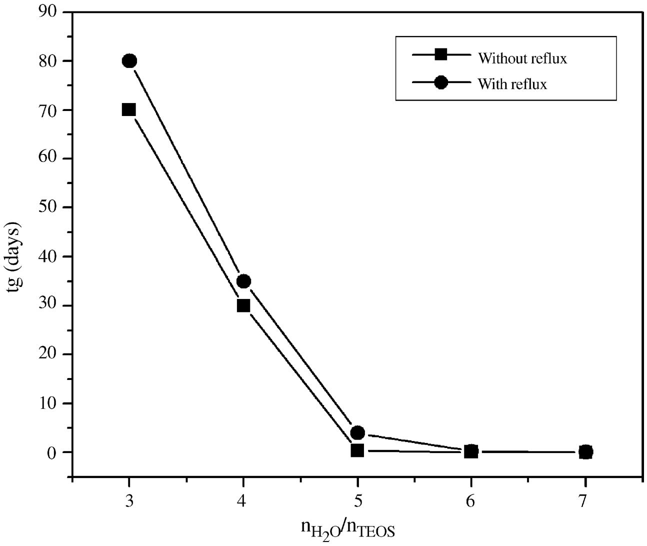

Fig. 3. Influence of the reflux on the time of gelation as a function of the molar ratio of hydrolysis.

The objective of the second preparation is to decrease the reactivity of TIP towards hydrolysis. One way to achieve this goal is to use acetic acid as modifying agent [17], thus we first mix 0.015 mol of TIP and TEOS in 7.19 ml of ethanol under reflux (80 °C) and under stirring during 8 h. After cooling we add a solution of water, acetic acid and ethanol (4 ml) with a molar ratio $[H_2O]/[HOAc] = 13$, dropwise and under vigorous stirring. The molar ratios $[H_2O]/[TEOS]$ and $[HOAc]/[TIP]$ after addition are 3 and 0.23, respectively. We call this preparation "sol B". Two main reactions involving HOAc take place in this system:

$$Ti(OPr^i)_4 + CH_3COOH \rightarrow Ti(OPr^i)_3OOCCH_3 + Pr^iOH \quad (1)$$

$$CH_3COOH + CH_3CH_2OH \rightarrow CH_3COOCH_2CH_3 + H_2O \quad (2)$$

The reaction of TIP with HOAc leads to the creation of a dimer composed of bridging and terminal OPr^i and bridging CH_3COO^- ligands [18]. This reaction combined with the steric effect of the acetate ligand decreases the efficiency of the hydrolysis reaction. The esterification reaction between HOAc and EtOH generates new water molecules thus increasing the molar ratio of hydrolysis. We note that the low level of HOAc (experimentally fixed) added lower the pH of the solution (pH 4.5) and is sufficient to avoid the precipitation of titanium compounds.

Another way to modify the titanium alkoxide is to use acetylacetone to react with TIP. Acetylacetone is known to lead to a chelated titanate in an equimolar mixture with TIP and to cause the coordination of Ti to increase from 4 to 5 [16] thus decreasing the hydrolysis of the Ti alkoxide:

$$Ti(OPr^i)_4 + H_3CCOCH_2COCH_3 \rightarrow Ti(OPr^i)_3H_3CCOCHCOCH_3 + Pr^iOH \quad (3)$$

In order to prepare this sol, called "sol E", we first mix 0.015 mol of the two alkoxides in EtOH (7.19 ml) under reflux

(80 °C) during 8 h. After cooling, acac is added ([TIP]/acac = 1) and the solution is stirred for 1 h, hydrolysis is then realized by a mixture of water and 2.65 ml of ethanol ($[H_2O]/[TEOS] = 3$).

In a fourth approach following the method proposed by Yoldas [5] we first hydrolyze the Si alkoxide in order to create silanol groups, which will react with the Ti alkoxide. This preparation is called ‘‘sol C’’. We thus realize the hydrolysis of TEOS (0.015 mol) in ethanol (3.72 ml) with 0.43 ml of a concentrated nitric (53 wt%) acid solution ($[H_2O]/[TEOS] = 1$) with a pH less than 1. After 1 h stirring at room temperature we add the solution of TIP (0.015 mol) in ethanol (3.04 ml) and let the mixture under reflux (80 °C) for 8 h. We then hydrolyze, after cooling, the mixture using a solution of water (0.54 ml) diluted in 4.46 ml of ethanol leading to a final ratio $[H_2O]/[TEOS] = 3$. The expected reactions occurring in the system are the following:

$$\mathrm{Si(OEt)_4 + H_2O \rightarrow Si(OH)(OEt)_3 + EtOH} \tag{4}$$

$$\mathrm{4Si(OH)(OEt)_3 + Ti(OPr^{\mathit{i}})_4 \rightarrow Ti[OSi(OEt)_3]_4 + 4Pr^{\mathit{i}}OH} \tag{5}$$

$$\mathrm{Ti[OSi(OEt)_3]_4 + 12H_2O \rightarrow -Si-O-Ti-O-Si- \; + \; 12EtOH} \tag{6}$$

The last preparation is based on the work presented by Yamane et al. [19]. In order to decrease the rate of hydrolysis of titanium isopropoxide they proposed to prepare titanium tetra(*tert*-amyl)oxide through the reaction of TIP with *ter*-amyl alcohol. Following the same route we propose to synthesize titanium *iso*-amyloxide that has also a highly branched alkyl group of large size and we thus expect the reduction of the hydrolysis rate. The alcohol exchange reaction:

$$\mathrm{Ti(OPr^{\mathit{i}})_4 + 4Am^{\mathit{i}}OH \rightarrow Ti(OPr^{\mathit{i}})_{4-x}(OAm^{\mathit{i}})_x + xPriOH} \tag{7}$$

is realized by mixing TIP (0.015 mol) and isoamyl alcohol (13.6 ml) under reflux (110 °C/3 h) in 19 ml of toluene. After evaporation of the solvent the new precursor is mixed with an equimolar quantity of TEOS (0.015 mol) in 5.39 ml of ethanol under reflux (80 °C/8 h), the resulting mixture is then hydrolyzed using a solution of water ($[H_2O]/[TEOS] = 3$) in 6 ml of ethanol. This last preparation is called ‘‘sol D’’.

Table 4
Quantity of products (g/ml) used for the five methods (see text for details)

	A	B	C	D	E
TIP	4.264/4.46	4.264/4.46	4.264/4.46	4.264/4.46	4.264/4.46
TEOS	3.125/3.35	3.125/3.35	3.125/3.35	3.125/3.35	3.125/3.35
ETOH	9.63/12.19	8.84/11.19	8.86/11.22	8.99/11.39	7.766/9.84
H_2O		0.81/0.81	0.54/0.54	0.81/0.81	0.81/0.81
HNO_3 (53%)			0.575/0.43		
acac					1.502/1.55
AcOH		0.198/0.19			
Am^iOH				10.578/13.06	

All the preparations are summarized in Fig. 4 and the quantities of the products used for the five methods are listed in Table 4.

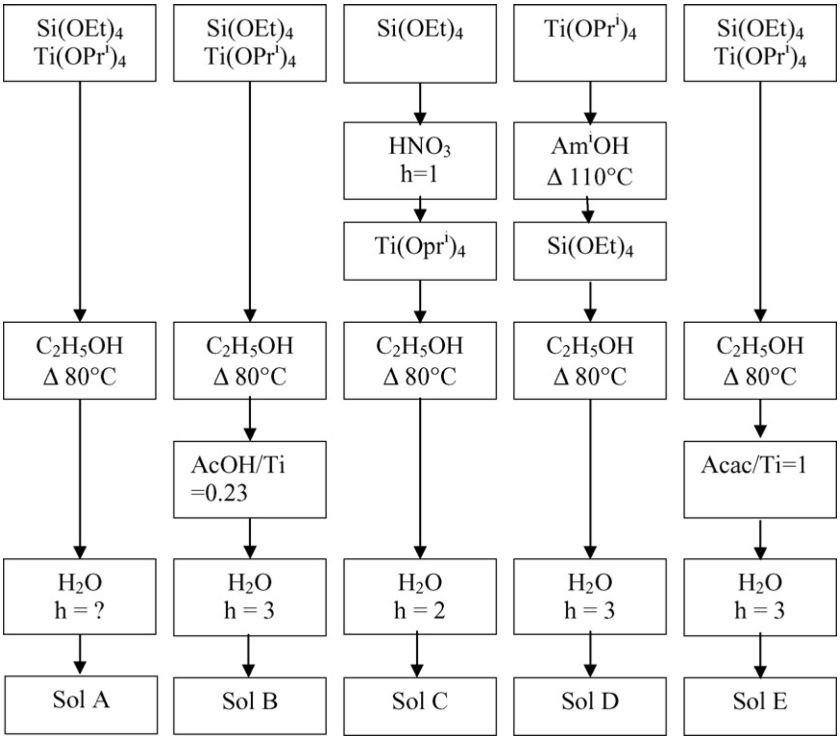

Fig. 4. Flow chart of the five sols preparation.

3. Results

3.1. Viscosity

Fig. 5 shows the evolution of the sol viscosity as a function of time for the five different preparations. As it can be seen the sol A evolves rapidly towards a high viscosity and transforms to a gel in 2 days. This behavior is surely due, for this sole preparation, to the evaporation of the solvent, which makes the concentration of the alkoxides increase. Sols B and D present the same evolution showing that the modification of the titanium alkoxide by acetic acid or isoamyl alcohol is efficient in order to prevent precipitation and to control the hydrolysis–condensation process. The curve corresponding to the sol C evidences the modification of the reactivity of the system when the silicon alkoxide is hydrolyzed before the mixing step. In this case, silanol groups (SiOH) compete with water molecules during the hydrolysis of the titanium alkoxide. Furthermore, the acidity of the solution being high ($pH < 1$) the kinetic of the hydrolysis reactions are favored while the condensation reactions are slowed down. The modification of TIP by acetylacetone is known to lead to the inhibition of the polymerization reactions [20] thus explaining the slow evolution of the viscosity of the sol E and the time of gelation observed.

3.2. Thermal analysis

The weight losses noted in the thermo-gravimetric curves for the xerogels A, B, C, D and E are, respectively, 26.9, 28.7, 32.6, 38.6 and 36.5%. The xerogels A, B and C mainly contain water ethanol and isopropanol which are low weight molecular compounds while xerogels D and E contain higher weight molecular groups leading to a higher weight loss during thermal treatment.

In the first range of temperature (20–350 °C) of the DTA curves we observe a first endothermic peak around 120 °C for all the samples. This peak is attributed to the vaporization of the physisorbed water and the organic solvent trapped in the porosity of the sample. One other weak endothermic peak is also noted for the xerogels D and E at 300 and 350 °C, respectively. This second peak may be attributed to the combustion of organic groups arising from isoamyl alcohol and acetylacetone. The combustion of the remaining alkoxy groups binded to titanium and silicon which result of the incomplete hydrolysis/condensation reactions can also contribute to these peaks. In the range 400–600 °C the DTA curve corresponding to the sole TiO_2 xerogel, obtained by the hydrolysis of TIP by acetic acid ([AcOH]/[TIP] = 3), displays a sharp and intense peak (415 °C) corresponding to the transformation of the amorphous oxide into the crystallized anatase phase. In this temperature range no peak is detected for the SiO_2–TiO_2 xerogels meaning that no crystallization of anatase occurs up to 600 °C. In Fig. 6 are presented the results of the differential thermal analysis of the five xerogels in the temperature range 600–700 °C. Broad and low peaks are detected for each xerogel ranging from 625 °C up to 660 °C. These peaks are due to the crystallization of the anatase phase in the mixed oxides systems and occur more than 200 °C above the crystallization temperature noted for the single titanium oxide system.

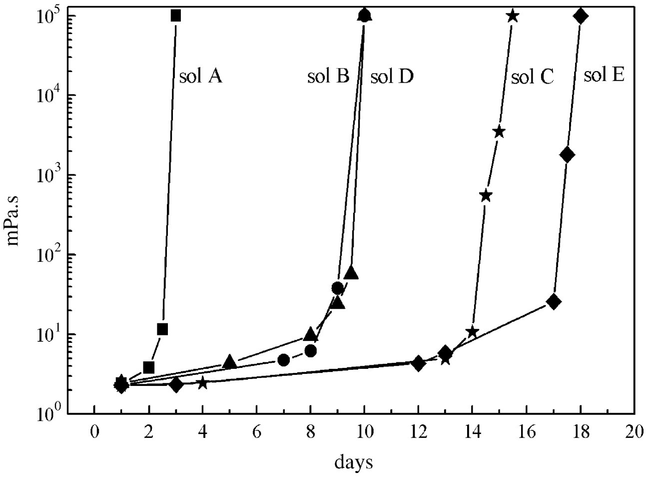

Fig. 5. Evolution of the viscosity for the five different preparations.

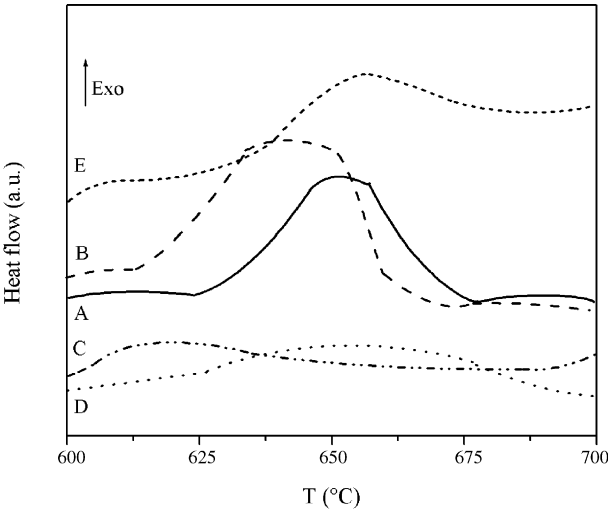

Fig. 6. DTA curves.

The dilatometric results show that the xerogels A, B and C present a linear shrinkage of 20, 16 and 18%, respectively, while the value of 28% is obtained for the xerogels D and E. Moreover, the dilatometric curves display a thermal expansion between 1150 °C and 1300 °C for the xerogels A–D, letting suppose a total densification in this temperature range, while no thermal expansion is noted for the xerogel E.

3.3. Infrared study

In Fig. 7 are presented the IR spectra obtained for the sol B at various temperatures. In this wave-number range all the xerogels present the same absorption bands. The bands located at 460 cm^{-1}, 800 cm^{-1}, 1050 cm^{-1} and 1250 cm^{-1} are attributed to the silica network [16,21] and the broad band (or shoulder) located between 660 cm^{-1} and 550 cm^{-1} is attributed to the Ti–O–Ti bond [22,23]. The Si–O–Ti bond is

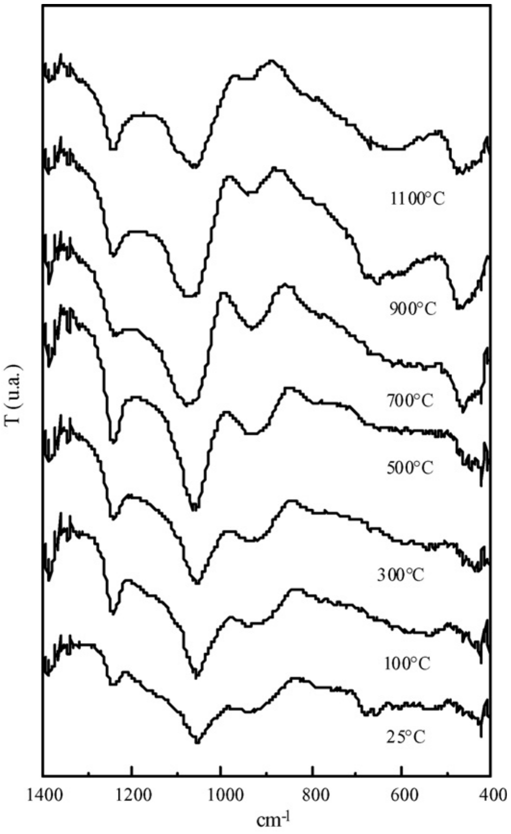

Fig. 7. IR spectra of sol B.

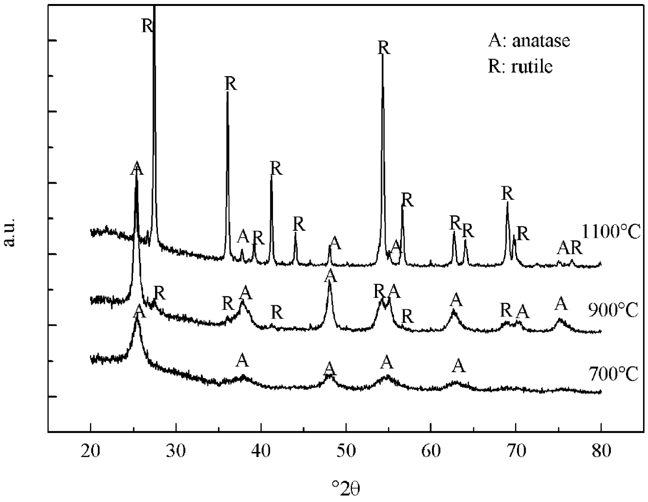

Fig. 8. X-ray diffraction patterns of xerogel A at various temperatures.

characterized by the absorption band around 930 cm^{-1} [22,24–26], this band can also be attributed to the Si–OH bond [16,27]. The band located at 945 cm^{-1} is observed for a silica xerogel obtained in acidic conditions, this band disappears when the xerogel is calcined at 500 °C while it is always present at 1100 °C for the mixed xerogels. The band attributed to the Ti–O–Ti vibration clearly appears at 900 °C for the mixed oxides xerogels. Concerning the silica network the band at 1050 cm^{-1} and 1250 cm^{-1} (LO and TO modes of the asymmetric stretching Si–O–Si vibration) are present for all the temperatures, the band located at 800 cm^{-1} (bending Si–O–Si vibration) appears as a shoulder at 900 °C for the mixed oxides systems while it is present since 25 °C for the silica gel and the band at 460 cm^{-1} (rocking Si–O–Si vibration) clearly appears at 500 °C for the mixed oxides while an intense band is detected since 25 °C for the silica gel.

3.4. X-ray diffraction

X-ray diffraction patterns of xerogel A calcined at 700 °C/3 h, 900 °C/3 h and 1100 °C/3 h are presented in Fig. 8. For temperatures lower than 700 °C and for all the mixed oxides powders, no diffraction peak is detected. In the range of temperature between 700 °C and 1100 °C the presence of TiO_2 anatase and rutile phases is observed while the brookite phase is never detected. Various published studies have already shown that in the SiO_2–TiO_2 system the temperature of anatase crystallization and the temperature of transformation from anatase to rutile depend on the synthesis way and on the Ti precursor content [4,17,28,29]. Higher is the SiO_2 content in the mixed system higher is crystallization temperature. To our knowledge no study describes the evolution of the content of anatase and rutile in the mixed system with the temperature.

We used a general model for the quantitative XRD analysis of the volume percent of anatase in a rutile–anatase mixture. The intensity of a diffraction peak of a chemical compound or phase is dependent on the structure and elements of the compound, the diffractometer characteristics, the absorption of X-rays by the sample and naturally on the concentration of the compounds in the sample (weight or volume fraction) which can be written as the following formula:

$$C_i = B_i(\mathrm{MAC})I_i^{\mathrm{net}} \tag{7}$$

where MAC is the mass attenuation coefficient for the sample, B_i a calibration factor, C_i and I_i^{net}, respectively, the concentration and the net intensity of the phase i diffraction peak. The calibration constant B_i is established by measuring reference samples with known concentrations of the analytical phases. The MAC values for compounds and mixtures are obtained by addition of the values for the elements according to their weight proportions. The net intensity is calculated using a linear background under the peak and subtracting the α_2 area to the total scan area. The MAC values for the anatase and rutile are within a very small range so the general model can be simplified in a linear expression. Thus, we have established the following formula for anatase–rutile with the concentration of anatase C_A expressed in volume percent:

$$C_A = \frac{8I_A}{13I_R + 8I_A} \tag{8}$$

where I_A is the [1 0 1] reflection of the anatase phase and I_R is the [1 1 0] reflection of the rutile phase. In Table 5, results of phase identification and volume percent of anatase phase are summarized. As it can be noted the highest anatase volume percent at 1100 °C is found for the sols C and D. We also study the evolution of the crystallites size for different thermal

Table 5
Results of the phase identification and the anatase volume percent for the xerogels calcined at different temperatures, A (anatase), R (rutile)

T (°C)/3 h	SiO_2	TiO_2	A	B	C	D	E
500	Amorphous	A A–R	Amorphous	Amorphous	Amorphous	Amorphous	Amorphous
700	Amorphous	7.5% A	A	A	A	A	A
900	Amorphous	R	A–R	A	A	A	A
1100	Amorphous	R	A–R 9% A	A–R 10.2% A	A–R 39.5% A	A–R 32.6% A	A–R 7% A

Table 6
Evolution of the crystallites size as a function of temperature, A (anatase), R (rutile)

T (°C)/3 h	TiO_2	A	B	C	D	E
500	A: 41 nm					
700	A: 84.5 nm R: 337 nm	A: 6.5 nm	A: 4 nm	A: 4.2 nm	A: 3.5 nm	A: 3.5 nm
900	R: 437 nm	A: 15 nm	A: 11 nm	A: 10 nm	A: 9.5 nm	A: 11 nm
1100	R: 777 nm	A: 98 nm R: 82 nm	A: 53 nm R: 57 nm	A: 49.5 nm R: 58 nm	A: 48 nm R: 48 nm	A: 39 nm R: 58 nm

treatments using the Scherrer relation, the results of this study are presented in Table 6. For all the mixed systems the anatase phase is present as a nanometer level up to 900 °C, thus these materials can be seen as nanocomposites where the major part of TiO_2 is embedded in an amorphous silica matrix.

4. Discussion

The results obtained in this work show that the route employed to synthesize TiO_2–SiO_2 materials strongly affect the characteristics of the final mixed oxide. Except for the IR analysis, which show the same metal–oxygen absorption bands for the five systems the other analysis lead to different results. Whatever the method employed mixed oxides are obtained, indeed no phase separation is detected using DTA or XRD below 625 °C meaning that TiO_2 is present as an amorphous state and surely mixed with the silica network at a nanometer level up to this temperature. Nevertheless, it seems difficult to claim that Ti, O and Si are mixed at the atomic level in the xerogels, which should be the ideal case, due to the presence of the absorption bands of the Si–O–Si bonds observed in the IR spectra since 25 °C. During the sol formation step, probably a fraction of Si and Ti atoms is linked by *oxo* bridges, as it has been evidenced using ^{17}O NMR spectroscopy [30], while the counterpart forms Si–O–Si and Ti–O–Ti oligomers and/or clusters. The resulting xerogels are then amorphous mixtures of silica, titania and mixed silica–titania.

As is evidenced in Fig. 5, the time of gelation is clearly different for the five preparations. We can thus expect different structures of the gels implying different ratios of Si–O–Ti bonds, different ratios of residual Si–OH and Ti–OH functions, more or less branched polymer like structure and so on. Indeed, the linear shrinkage of the gels is more pronounced for the xerogels D and E than for the others letting suppose a less dense structure at the initial stage (dried gel). Moreover, among the five xerogels and according to the dilatometric results the only one that seems to be not fully densified at 1300 °C is the xerogel E. The broad peaks observed in DTA (Fig. 6) can be due to the breakage of the Si–O–Ti bonds, which occurs with or just before the crystallization of the anatase. All the crystallization peaks are observed in the range 625–660 °C following the sequence C, B, A, D, E with some difference in their shapes. Peaks concerning the xerogels A and B are better defined and more intense than the others in part due to the fact that these xerogels have lost less weight than the others. One of us have already observed [7] an increase of 200 °C of the crystallization of ZrO_2 in the mixed system ZrO_2–WO_3, in this study where the tungsten oxide was supposed to cover the ZrO_2 particles, the peak detected in the DTA was as narrow and as intense as the peak detected for the sole zirconium oxide. In the present study, the large DTA peak could arise from the distribution of the Si–O–Ti bonds which are surely present not only in a mixed network but also at the interface between the silica and titania network and inside the titania and the silica clusters. These different localizations lead to different energies and kinetics for the demixion/crystallization phenomenon and make the DTA peaks to have a low intensity and to spread over a large range of temperature. This behavior expresses the non-homogeneity of the material in its amorphous state. As it can be seen in Tables 5 and 6 the titanium oxide behaves in a different way with and without the presence of the SiO_2 phase. For the sole titanium oxide system the classical scheme of transformation with temperature is respected, i.e. the crystallization of the anatase phase occurs below 500 °C the transformation of the anatase into rutile takes place around 700 °C and finally coalescence of crystallites are observed up to 1100 °C that is the highest temperature used in this study. In the case of a SiO_2–TiO_2 (1:1) system this scheme has completely changed, no diffraction peak is revealed before 700 °C, the anatase phase is present up to 1100 °C and the crystallite size do not exceed 60 nm except for the xerogel A. Various factors can contribute to prevent the crystallization below 620 °C and the phase transformation at higher temperatures:

- The amorphous matrix acts as a barrier for the crystallization and the phase transformation.
- The surface energy associated with the amorphous cluster size and the anatase crystallite size can stabilize the microstructure.
- The presence of silicon atom trapped in the titanium oxide network can hinder the crystallization and the phase transformation.

The presence of the rutile phase since 900 °C and the important grain growth noted for the xerogel A can arise from the less efficient formation of Si–O–Ti bond in the titania network that can be linked to the low time of gelation. The preparations C and D are the most appropriate to keep the titania anatase phase at high temperature while the preparation E seems to be the least appropriate. It is possible that this last preparation generates a great porosity explaining that this xerogel seems to be not fully densified at 1300 °C and that the silica matrix effect is less efficient to avoid the apparition of the rutile phase at 1100 °C.

5. Conclusion

We have succeeded in preparing translucent gels following five different routes. The infrared spectroscopy evidences the presence of Si–O–Ti bonds from the room temperature up to 1100 °C. Nevertheless, Si–O–Si absorption bands are also revealed implying the presence of a silica network since 25 °C. The crystallization of the anatase phase inside the mixed oxides occurs more than 200 °C above the temperature observed for the crystallization when the sole titanium oxide is studied indicating a strong interaction between the two oxides. The anatase crystallites size is less that 15 nm at 900 °C for all the xerogels and the preparation C (pre-hydrolyze of the silica alkoxide) and D (modification of the titanium alkoxide by isoamyl alcohol) are the most appropriate to keep the titania anatase phase at high temperature while the preparation E (modification of the titanium alkoxide by acetylacetone) seems to be the least appropriate.

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