

THERMAL STABILITY OF SiO₂-BASED INORGANIC-ORGANIC HYBRID MATERIALS

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Abstract

The hydrolysis-polycondensation of organically modified Si-alkoxides leads to the obtaining of inorganic-organic hybrid materials in which the organic moieties remain as permanent groups bonded to the inorganic network.

The molecular species previously determined by GC-MS during the gelation process have been significantly different according to the type of the alkoxide used.

In the present work, thermal stability of SiO₂-based inorganic-organic hybrid materials starting with TEOS (tetraethoxysilan), MTEOS (triethoxymethylsilan), VTEOS (triethoxyvinylsilan) and MTMOS (trimethoxymethylsilan) was studied.

The molecular structure of the gels obtained determines differences in their thermal behaviour. Gels obtained starting with MTEOS show the highest thermal stability, while gels obtained using VTEOS the lowest, among the substituted alkoxides. A particular behaviour presents the gel obtained with MTMOS that decomposes in four steps. This could be explained by the presence in the gel of some prevalent types of molecular species with different thermal stability.

Keywords: inorganic-organic hybrids, molecular species, thermal analysis

Introduction

In the past decade, a great deal of research and development was carried out on the preparation of crystalline and non-crystalline ceramic oxides by sol-gel method. Besides the large volume of work conducted on purely oxide systems, there were many attempts to incorporate organic materials into sol-gel-derived oxides, resulting in the inorganic-organic hybrid materials. These can be conveniently divided into two groups:

In the first group, materials with no primary chemical bonds between the oxides and organics are included. In the second group the oxides and the organics do form chemical bonds with one another, being obtained by hydrolysis-polycondensation of organically modified alkoxides [1].

In a previous work the hydrolysis-polycondensation of some organically modified Si-alkoxides was studied by using GC-MS and IR spectrometry [2]. Depending

on the type of the alkoxide used, significant differences were noticed, both in the reaction rate and in the molecular species formed during the sol-gel process.

The gels obtained with different Si-alkoxides present also significant differences due to the organic moieties bonded to the inorganic network. Differences in the structure of the obtained gels will lead surely to differences in their properties.

In the present paper the thermal stability of SiO₂-based inorganic-organic hybrid materials starting with tetraethoxysilan (TEOS) triethoxymethylsilan (MTEOS), triethoxyvinylsilan (VTEOS) and trimethoxymethylsilan (MTMOS) was studied.

Experimental

Samples preparation

As Si-precursors the following alkoxides were used: tetraethoxysilan (TEOS), triethoxymethylsilan (MTEOS), triethoxyvinylsilan (VTEOS), trimethoxymethylsilan (MTMOS), all Merck.

All starting solutions had the same molar ratio: Si-alkoxide/H₂O/EtOH=1/1/1.75 (HCl as catalyst, pH=3.5).

The samples were stored in closed glass vials and subjected to GC-MS and IR spectrometry runs at different times.

A double focus 70-SE VG Analytical Mass Spectrometer coupled with Hewlett-Packard 5890 Gas Chromatograph was used under the experimental conditions presented elsewhere [3, 4]. The areas of the molecular species detected by GC were automatically integrated by a PKD special program or using the data system display of the GC-MS equipment.

Gels were obtained by quick evaporation of the solvent from the sample similar to those used for GC-MS and IR spectrometric investigations.

Samples characterisation

The XRD patterns were recorded on a FPM HZ-4 diffractometer using CuK_α radiation with Ni filter.

The FT-IR spectra were recorded on a Perkin Elmer IR System 2000 equipment, in the 4000–400 cm⁻¹ range. Measurements were made in solid phase using KBr pellets.

Thermal analysis was performed up to 1000°C using a MOM Budapest type Paulik-Paulik-Erdey derivatograph OD-102. The measurements were carried out in static air atmosphere with α-Al₂O₃ as reference at a heating rate of 5°C min⁻¹.

The Evolved Gas Detection (EDG) analysis was realised on a DuPont 916 Thermal Evolution Analyser with hydrogen-flame ionisation detector, in purge gas N₂ at 1.8 l h⁻¹ at a heating rate of 8°C min⁻¹.

Results and discussion

Previous GC MS and IR studies, published elsewhere [2] have shown that the sol-gel process is very complex and many different intermediates could be formed. That means is very hard to give an exact thermodynamical description of what might

Table 1 Molecular species identified at 96 h from the start of the sol-gel reactions

Species	TEOS	MTEOS	VTEOS	MTMOS
H ₂ O	9584	–	6870	2122
R-OH	109410*	100000*	142594*	69034**
Alkoxides	95068	9246	21713	51839
MO	100179	2774	6917	5219
M ₂ O	–	90000	–	–
D	120700	152799	141016	122239
DO	186209	60000	159905	244467
D ₂ O ₁	–	–	50279	–
D ₂ O ₂	–	4277	–	–
CT	20762	26042	21482	334
CT ₂	–	66175	63859	1850
CTO	22737	363	80987	–
CT ₂ O ₁₋₂	–	–	13448	105
LT	89049	8916	122808	160560
LT ₁ O _x	112816	2531	84082	44197
LT ₂ O _x	19283	94421	1053	–
CTET _x	9774	–	89000	83917
CTETO	20277	–	74000	875
BCTET	21114	470	7000	–
BCTETO _x	9370	94491	–	–
BTET	8940	–	11967	38500
BTETO	6542	1106896	–	–
LTET	59801	28397	111193	129300
LTETO _x	17650	24401	–	–
CP _x	786	23700	12500	100191
BP	–	–	36059	–
R1CP	4083	–	–	–
B1CPO _x	4570	–	–	–
B _x CP	6832	–	–	–
B1PO	1342	–	–	–
B1LP	–	–	–	43093
LP	8531	–	–	77736
LPO	3063	–	–	–

Table 1 Continued

Species	TEOS	MTEOS	VTEOS	MTMOS
B1CHx	416	–	–	9393
CH	–	72390	5709	57845
BxH	–	–	–	28696
LH	–	–	–	47728
HEP	–	28923	–	–
B1CHEPx	–	–	–	4035
CHEP	–	–	–	24089
BxHEP	–	–	–	20299
LHEP	–	–	–	25606
COCTx	–	–	–	11950
B1COCT1	–	–	–	8767
B2COCT2	–	–	–	8953

Legend: *Et-OH, **MeOH, M – monomer, D – dimer, T – trimer, TET – tetramer, P – pentamer, H – hexamer, HEP – heptamer, OCT – octamer, MO – hydroxylated monomer, DO – hydroxylated dimer, C – cyclic, L – linear, B – branched

be possible or not in these complicated reaction paths. As a consequence, it is not possible to give detailed thermodynamically based prognoses and the effect of different reaction parameters (type of alkoxide, solvent, catalyst, temperature, concentration) has to be investigated experimentally and the conclusions have to be drawn from these results.

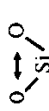
More detailed investigations of sol-gel systems in which only the initial alkoxide differs show significant changes both in the rate of reactions and in the molecular species obtained at different times of reactions. In Table 1 GC-MS results obtained after 96 h from the start of the reaction are presented.

One may notice that in the case of tetraethoxysilan (TEOS) the preponderant species are the monohydroxylated monomer, dimers and linear trimers, still high amount of monomer being noticed. In the case of MTEOS, molecular species with higher degree of polymerisation are predominant, tetramers and in less amount pentamers. In the solution prepared with VTEOS, dimers, trimers and tetramers are identified as predominant molecular species. From this point of view, VTEOS ranges between TEOS and MTEOS. The predominant molecular species identified in the solution obtained starting with MTMOS are dimers, trimers, tetramers and pentamers.

The differences in the molecular species present in the studied sol-gel solutions, before gelation, are connected with both alkoxy groups and the type of organic substituents of alkoxides. All analysed solutions led, by quick evaporation, to gels with practically the same molecular species in their structure as those presented in Table 1.

All gels were amorphous as determined by XRD. However, the FT-IR spectra of the gels are different.

Table 2 Assignment: of the vibration bands in the FT-IR spectra of the gels obtained starting with: TEOS, MTEOS, VTEOS, VTEOS and MTMOS

Vibration modes	Wavenumbers/cm ⁻¹				Assignments
	TEOS	MTEOS	VTEOS	MTMOS	
νOH	3446 s b	3440 s b	3435 s b	3446 s s	Si-OH
ν(=CH ₂)/ν(=CH)	-	-	3065 w	-	Si-CH=CH ₂
ν _a CH ₃	-	2985 w	-	2976	Si-CH ₃
ν _a CH ₂	-	-	2961 w	-	Si-CH=CH ₂
ν _s CH ₃ /ν _s CH ₂	-	2920 vw	2850 vw	2846 vw	Si-CH ₃
δHOH	1639 m	1650 m	1640 sh	1633 w	
νC=C	-	-	1604 m	-	Si-CH=CH ₂
δ _a CH ₃	-	1460 m	-	1450 vw	Si-CH ₃
β _s (=CH ₂)/β(=CH)	-	-	1411 m	-	Si-CH=CH ₂
δ _s CH ₃	-	1400 w	-	1412 vw	Si-CH ₃
ν _{as} Si-O-Si LO	1220 sh	1275 m	1278 m	1275 m	cyclic species
ν _{as} Si-O-Si TO	1088 vs	1130 vs	1127 vs	1125 vs	linear species
ν _{as} Si-O-Si TO	-	1030 vs	1046 vs	1030 vs	Si-CH=CH ₂
ν(=CH ₂)/ν(=CH)	-	-	1007 m	-	Si-OH
νSi-O(H)	937 m	970 w	966 w	950 sh	Si-CH ₃
rSi-C	-	850 m	-	855 vw	T1 of SiO ₄
ν _s Si-O-Si/νSi-C	791 s	780 vs	766 s	767 vs	cyclic tetramers
ν _s Si-O-Si	568 m	550 m	545 m	561 mb	Deformation of angle
δSi-O-Si	462 vs	420 s	435 s	420 s	

The assignment of the IR vibrations is presented in Table 2. The gel obtained starting with TEOS presents all the IR vibration bands reported by Bertoluzza *et al.* [5] for the SiO₂ gels. The IR spectra of the gels obtained with MTEOS and MTMOS are different compared to IR spectrum of the gel obtained with TEOS. They show, besides the bands corresponding to Si–O and Si–OH vibrations, the characteristic vibrations of the –CH₃, Si–CH₃ [6], confirming that the gels contain significant amount of organic part. The gel obtained starting with VTEOS present beyond the groups mentioned for the gels prepared starting with MTEOS and MTMOS, vinyl C–H stretching and deformation and C=C stretching vibration bands.

The TG/DTG curves corresponding to the obtained gels are presented in Fig. 1.

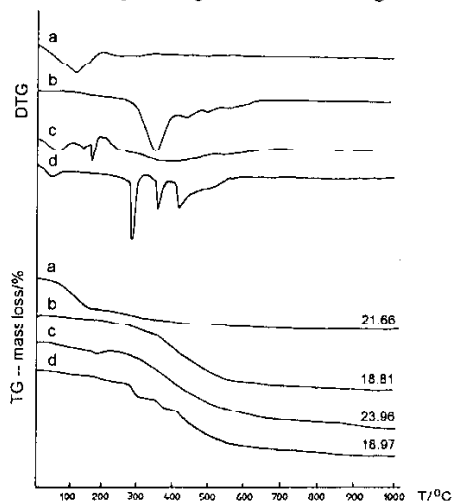


Fig. 1 TG/DTG curves of the obtained gels starting with: a – TEOS, b – MTEOS, c – VTEOS, d – MTMOS

Differences in the temperatures of thermal decomposition and in the weight losses are noticed. A comparative discussion of the TG/DTG results and those obtained by Evolved Gas Detection by hydrogen flame ionisation led us to the following conclusions:

The gel obtained starting with TEOS behaves practically as a common silica xerogel. It starts its decomposition at about 80°C and no organics evolution was noticed.

The gel obtained with MTEOS is stable up to about 400°C, then it decomposes in a single step, with a significant amount of organics evolution. The behaviour is that of an organic modified silica gel. The slow and prolonged weight loss on TG curve could be connected to the smaller endothermal effects on the DTG curve.

The gel obtained with VTEOS presents a thermal stability ranging between that of the gel obtained with TEOS and that of the gel obtained with MTEOS. In this case the gel keeps its mass until about 200°C, when a slow weight gain is observed, which could be assigned to the oxygen uptake process on the vinyl groups. That process

may accelerate the burning out of organics. Significant evolution of organics is noticed from 350°C. The slow oxidation of the vinyl group could be an explanation of the lowest thermal stability of this gel.

The gel obtained with MTMOS has a specific behaviour. Its weight is constant till 300°C; then, the weight loss takes place stepwise, in four defined stages, according to DTG curves. On the TG curve the two last stages overlap. Significant amount of organics release between 400 and 500°C was noticed.

For explaining the different thermal stability of the obtained gels, an attempt to correlate the thermal behaviour with the molecular species present in the solution at the moment of gelation, was made.

The high thermal stability of the gel obtained starting with MTEOS could be explained by the presence in the structure of the gel of practically one predominant molecular species, the branched hydroxylated tetramer, with a defined and rather high thermal stability (Table 1). The smaller endothermal effects on the TG curve could be connected to the presence in less extent of the pentamers.

The low stability of the gel obtained starting with VTEOS could be explained both by the presence in the structure of the gel of a higher number of predominant molecular species with lower degree of polymerisation and by the low thermal stability of the vinyl groups bonded to the silica network.

The specific behaviour of the gel obtained starting with MTMOS could be explained by the presence in the gel of some prevalent types of molecular species with different and specific thermal stability (dimers, linear trimers, linear tetramers, linear and cyclic pentamers).

It is worth mentioning, that previous papers have reported results concerning the thermal stability of some inorganic-organic hybrid gels. They refer, especially to gels belonging to the first group of hybrid gels, in which no primary chemical bonds between the oxides and organics occur. In such gels the thermal stability is determined by that of the individual components [1, 7]. Complex gels obtained from mixtures of highly substituted alkoxides were also studied [8–10].

Conclusions

The thermal stability of SiO₂-based inorganic-organic hybrid materials starting with tetraethoxysilan (TEOS), triethoxymethylsilan (MTEOS), triethoxyvinylsilan (VTEOS) and trimethoxymethylsilan (MTMOS) was studied.

Starting with the mentioned alkoxides, gels with different structure were obtained depending both on the alkoxy group and on the organic substituent of the alkoxides.

The thermal stability of the obtained gels is strongly influenced by the molecular species formed during the gelation process.

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