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AGEING EFFECT ON THE SiO_2-BASED INORGANIC–ORGANIC HYBRID MATERIALS

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Abstract

It is well known that SiO_2-based inorganic–organic hybrid materials present significant differences due to the organic moieties bound to the inorganic network and to the preparation conditions.

In the present work the ageing effect on the thermal stability of the SiO_2-based inorganic–organic hybrid materials prepared using tetraethoxysilan (TEOS), triethoxymethylsilan (MTEOS), triethoxyvinylsilan (VTEOS), tetramethoxysilan (TMOS), trimethoxymethylsilan (MTMOS) and trimethoxyvinylsilan (VTMOS) was studied.

TG/DTA-MS was used to study the decomposition process of the materials. The structural modifications of the materials during ageing were studied using spectral methods.

The gels obtained starting with more reactive alkoxides, of methoxy-type, present more complex structures and are less stable during ageing.

Keywords: ageing, inorganic–organic hybrids, IR spectrometry, thermal analysis, TG-DTA

Introduction

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 inorganic–organic hybrid materials. Generally, significant differences due to the organic moieties bound to the inorganic network and to the preparation conditions were noticed [1, 2].

In a previous work [3] the thermal stability of SiO_2-based inorganic–organic hybrid materials prepared from tetraethoxysilan (TEOS), triethoxymethylsilan (MTEOS), triethoxyvinylsilan (VTEOS) and trimethoxymethylsilan (MTMOS) was studied.

Starting with the mentioned alkoxides, gels with different structures were obtained depending both on the alkoxyl group and on the organic substituents of the alkoxides [4, 5].

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The thermal stability of the obtained gels was strongly influenced by the molecular species formed during the gelation process [3].

In the present work the effect of ageing on the thermal stability of the SiO_2-based inorganic–organic hybrid materials synthesized from tetraethoxysilan (TEOS), triethoxymethylsilan (MTEOS), triethoxyvinylsilan (VTEOS), tetramethoxysilan (TMOS), trimethoxymethylsilan (MTMOS) and trimethoxyvinylsilan (VTMOS) was approached.

Experimental

Sample preparation

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

All starting solutions had the same molar ratio:

Si-alkoxides/H_2O/EtOH=1/1/1.75 (HCl as catalyst, pH=3.5).

The samples were stored in covered glass vials and left for gelling at room temperature. The as prepared gels were kept for ageing for 6 and 9 months and were subjected to structural and thermal characterizations.

Sample characterization

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

IR spectra were recorded on a Carl Zeiss Jena Specord M80 equipment, in the 4000–200 cm^{-1} range. Measurements were made in solid phase using KBr pellets.

Thermal analysis was performed up to 1000°C using a STD 2960 simultaneous TG-DTA (TA Instruments), Thermostar-Quadrupol MS with Quadstar 422 software (Balzers Instruments); heating rate: 10°C min^{-1}; flowing air atmosphere: 10 l min^{-1}.

Results and discussion

The gels obtained from different alkoxides, in similar reaction conditions, have presented different times of gelation (Table 1). All obtained gels were amorphous, as shown by X-ray diffraction. However, the IR spectra of the gels are different due to the different molecular species existing in the final gels.

The assignment of the IR vibrations is presented in Table 1. The gel obtained from TEOS presents all the IR vibration bands reported by Bertoluzza *et al.* [6] for the SiO_2 gels.

The IR spectrum of the gel obtained from TMOS is different as compared to that of the gel obtained starting with TEOS showing, besides the bands corresponding to Si–O and Si–OH vibration, the characteristic vibrations of the $–Si–O–CH_3$ bond [7]. The specific absorption bands at 2960 and 2860 cm^{-1}, due to the asymmetric and symmetric vibrations of the $–CH_3$ group, are evident. In the same time the specific rock-

Table 1 Assignment of the vibration bands in IR spectra of the gels obtained starting with TEOS, MTEOS, VTEOS, TMOS, MTMOS and VTMOS

Vibration mode	Wavenumber/cm^{-1}						Assignments
	TEOS	MTEOS	VTEOS	TMOS	MTMOS	VTMOS	
νOH	3450 s,b	3430 s,b	3440 s,b	3450 s,b	3480 s,b	3440 s,b	Si–OH
ν(=CH_2)	–	–	3070 m	–	–	3070 m	Si–CH=CH_2
ν(=CH)	–	–	3020 vw	–	–	3030 w	Si–CH=CH_2
$\nu_{as}CH_3$	–	2985 w	–	2960 m*	2985 w	2960 m*	Si–CH_3, *Si–O–CH_3
ν_sCH_2	–	–	2970 w	–	–	2970 sh	Si–CH=CH_2
ν_sCH_3/ν_sCH_2	–	2930 vw	2860 vw	2860 m*	2930 vw 2860 m*	2860 w	Si–CH_3, *Si–O–CH_3
δHOH	1630 w	1640 w	1640 w	1650 vw	1630 vw	1650 vw	H_2O
νC=C	–	–	1610 m	–	–	1610 m	Si–CH=CH_2
δ_{as}C–H	–	1410 vw	–	1460 w	1420 vw	–	Si–CH_3, Si–O–CH_3
δ(=CH_2)/δ(=CH)	–	–	1415 m	–	–	1415 m	Si–CH=CH_2
δ_sC–H	–	1280 s	1290 w	–	1280 s	1280 w	Si–CH=CH_2, Si–CH_3, *Si–O–CH_3
ν_{as}Si–O–Si LO	1170 s,br	1130 s,br	1140 s	1160 sh	1120 vs	1130 s	–Si–O–Si–
ν_{as}Si–O–Si TO	1060 s, br	1025 s,br	1050 s,br	1080 s,br	1030 vs	1040 s,br	–Si–O–Si–
γ(=CH_2)	–	–	1010 s	–	–	1010 s	Si–CH=CH_2
νSi–O–(H)	940 m	–	970 vw	940 sh	–	970 w	–Si–O–H
γ(=CH)	–	–	900 m	–	–	900 m	Si–CH=CH_2
rCH_3,*+ν_s–Si–O–Si–	–	850 sh	–	840* vs	850 sh	–	Si–CH_3, *–Si–O–Si–, Si–O–CH_3
ν_s–Si–O–Si–/ν_{as}C–Si	780 m	785 s 770 s	770 s	–	780 s 770 s	770 s	–Si–O–Si–, Si–CH_3, Si–CH=CH_2
ν_sC–Si	–	670 sh	690 w	–	680 w	690 w	Si–CH_3, Si–CH=CH_2
νSi–O–Si+ω(CH=CH_2)	580 m	550 m	540 s	570 m,br	550 s	540 m	cyclic tetramers
δSi–O–Si	440 vs	410 vs	435 m	450 s	420 vs	440 m	deformation of angle O–Si–O
Gelling time (h)	240	504	408	95	96	192	–

ν – streching, δ – deformation, r – rocking, ω – twisting, s – symmetric, as – asymmetric, vs – very strong, s – strong, m – medium, w – weak, vw – very weak, br – broad, sh – shoulder ing vibration sharp peak of methyl groups at 840 cm^{-1} overlaps the stretching symmetric –Si–O–Si– band at about 800 cm^{-1}.

This fact could be explained by the high reactivity of the methoxy-type alkoxides that determines a faster gelation process that leads to entrapment of partially hydrolysed monomers and oligomers in the final gel.

The IR spectra of the gels obtained with MTEOS and MTMOS present also, besides the bands corresponding to SiO_2 network, the characteristic vibrations of the $–CH_3$, $Si–CH_3$ [7, 8], confirming that the gels contain significant amount of organic part. In the case of the gels obtained from VTEOS and VTMOS, IR spectra present, beyond the groups mentioned for the gels prepared starting with MTEOS and MTMOS, vinyl $=CH_2$ stretching and deformation and C=C vibration bands.

The TG/DTA curves corresponding to the obtained gels are presented in Figs 1–3.

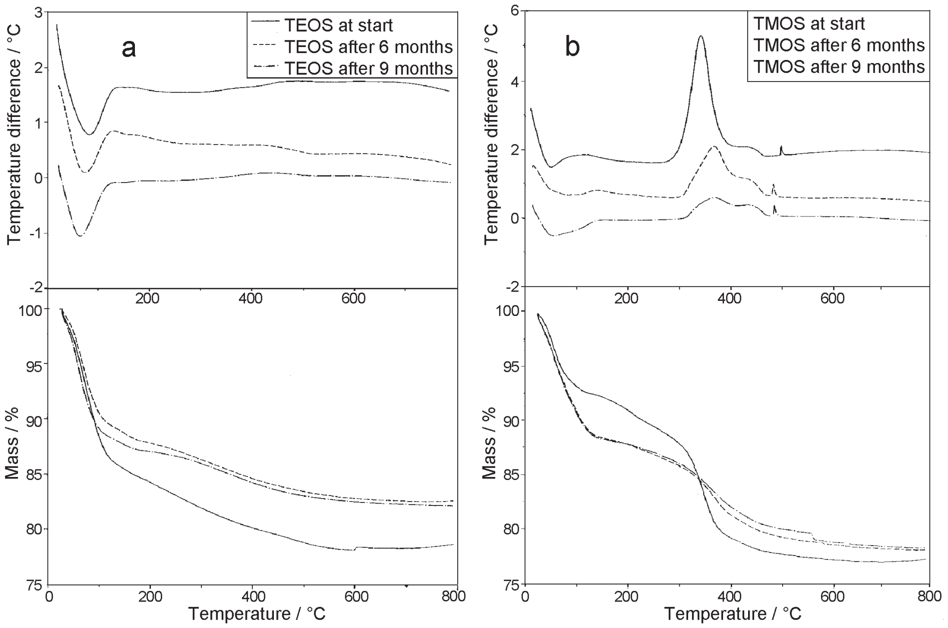

Fig. 1 TG/DTA curves of gels obtained at different ageing periods starting with a – TEOS; b – TMOS

Differences in the temperatures of thermal decomposition and in the mass losses are noticed, which could be explained by the presence in the structure of the gels of different molecular species, exhibiting different thermal stability [3].

The gel obtained from TEOS (Fig. 1a) behaves practically as a common silica xerogel. Water and/or solvent evolution started at about 80°C and no organics evolution was noticed up to 500°C.

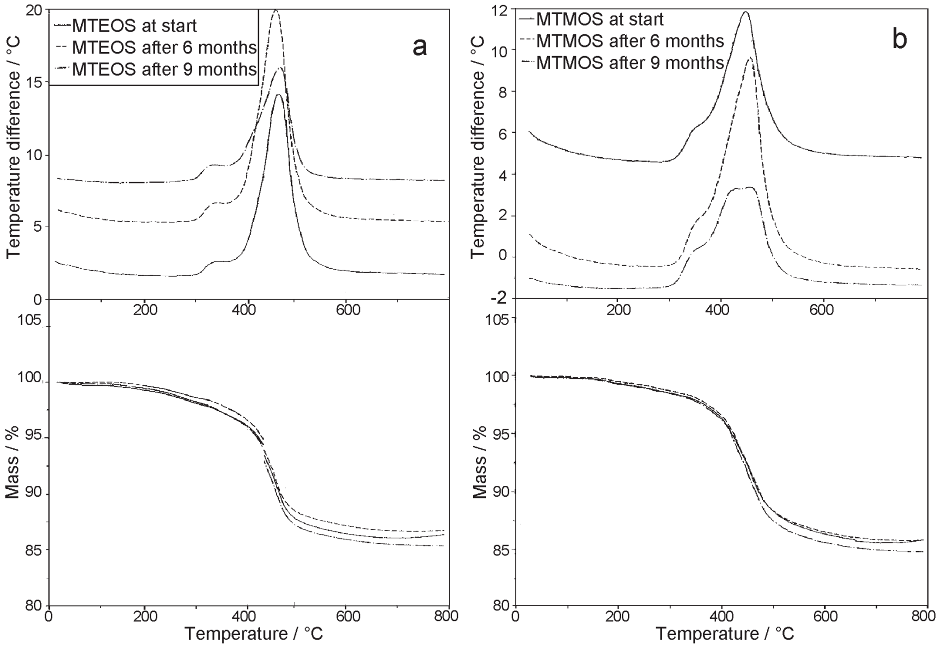

Fig. 2 TG/DTA curves of gels obtained at different ageing periods starting with a – MTEOS; b – MTMOS

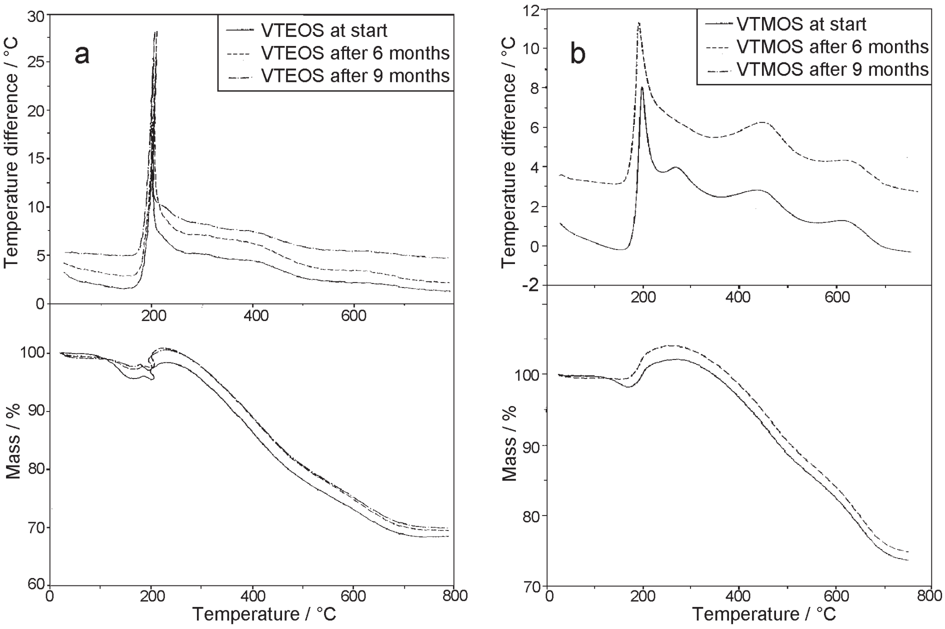

Fig. 3 TG/DTA curves of gels obtained at different ageing periods starting with: a – VTEOS; b – VTMOS

The gel obtained from MTEOS (Fig. 2a) is stable up to about 350°C, then it decomposes with a significant amount of organics evolution over 400°C. The decomposition is accompanied by two exothermal effects, due to the burning out of the organic radicals bound on the inorganic network. The behavior is that of an organic modified silica gel.

The main mass loss at 400°C could be explained by the presence in the structure of the gel of practically one predominant molecular species, which was previously determined by GC-MS [3] as being the branched hydroxylated tetramer with a defined thermal stability [3].

By ageing, the mass loss and the temperature of decomposition did not change essentially. However, the main DTA peak recorded after 9 months becomes larger. That could be explained by a more complex structure of the gel obtained as a result of a low temperature polycondensation process, which may continue at room temperature during ageing.

The gel obtained from VTEOS (Fig. 3a) presents a thermal stability ranging between that of the gel obtained from TEOS and that starting with MTEOS. In this case over 150°C a peculiar increase, decrease and increase again of the mass is noticed. This behavior could be assigned to the oxygen uptake process of the vinyl groups leading to some intermediates with specific thermal behavior. The process may accelerate the burning out of organics. Significant evolution of organics is noticed starting with 200°C.

By ageing, no significant changes in the thermal behavior of the gels obtained was observed,confirming that their structure is stable at room temperature.

The thermal behavior of the gel obtained from VTEOS, in the 100–250°C temperature range, needs further investigations.

The gel obtained from TMOS (Fig. 1b) presents different TG/DTA curves as compared with the gel obtained with TEOS (Fig. 1a). Besides the evolution of water and solvent, at about 80°C, a decomposition of the gel over 300°C was noticed. The DTA effect connected to the decomposition is exothermal, showing that a burning out of the organics takes place. The observed behavior is in good agreement with the IR data presented in Table 1.

By ageing, the DTA peaks are shifted to higher temperature and their height decrease. This could be explained by further development of the poly-condensation process at room temperature during ageing, which leads to more stable molecular species, with higher degree of polymerisation.

In the case of the gel obtained from MTMOS (Fig. 2b) a similar thermal behavior was noticed during ageing.

The influence of ageing on the thermal stability of the gels obtained from methoxy-type alkoxides could be correlated with the changes in the structure of the gels. In Fig. 4 the evolution of the IR spectra of the gels obtained from TMOS during ageing is presented.

The IR spectra, presented in Fig. 4, show the disappearance of the characteristic absorption bands of the methyl groups (2969 and 2860 cm^{-1}) during ageing. The sharp band characteristic of $-CH_3$ rocking vibration at about 840 cm^{-1}, which overlaps the Si–O–Si stretching vibration vanishes during ageing. Thus, after nine months the spectrum of pure silica xerogel was obtained. It could be concluded that poly-condensation developed in the solid phase during ageing.

The thermal stability of the gel obtained starting with VTMOS (Fig. 3b) is close to that obtained starting with VTEOS. However, the peculiar thermal effects observed around 200°C for the gel obtained with TEOS are not evident in this case. Only an increase of mass about 200°C is noticed that could be assigned to an oxygen uptake on the double bond of the vinyl group. Above this temperature the decomposition takes place step-wise being accompanied by exothermal effects due to the burning out of the organic residues.

The mass-spectrometric investigations could not detect any evolved gaseous products at this type of samples. The ion-fragments identified by mass spectrometry correspond to some oxidation products due to the fact that the measurements were carried out in air. No extra gases like ethylene, ethanol were detected.

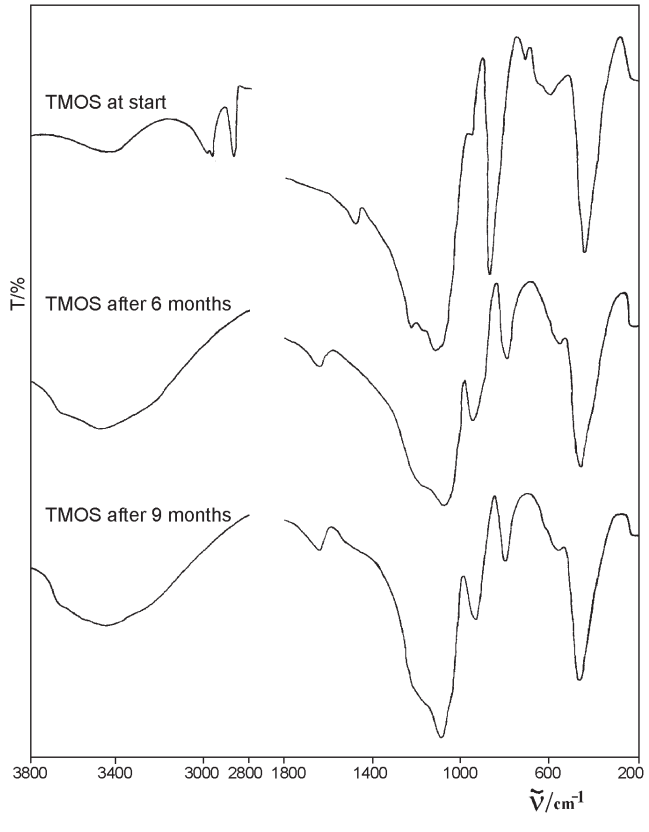

Fig. 4 IR spectra of the gel obtained starting with TMOS at different ageing periods

Conclusions

The effect of the ageing on the thermal stability of the SiO_2-based inorganic–organic hybrid materials obtained from tetraethoxysilan (TEOS), triethoxymethylsilan (MTEOS), triethoxyvinylsilan (VTEOS), tetramethoxysilan (TMOS), trimethoxymethylsilan (MTMOS) and trimethoxyvinylsilan (VTMOS) was studied.

In similar experimental conditions the structure of the gels and, consequently, their thermal stability is strongly influenced by the type of the alkoxides used as precursors in the sol-gel preparation.

The gels obtained using more reactive alkoxides, of methoxy-type, present more complex structures and are less stable during ageing.

In these cases, by ageing, further development of the poly-condensation process at room temperature takes place, which leads to molecular species with higher degree of polymerisation and with higher thermal stability.

The gel obtained from VTEOS presents a peculiar behavior that requires further investigations.

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