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Thermochemical behaviour of Ru(II) complex–SiO_2 microcomposites

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Abstract. The results from DSC and thermogravimetric analysis of gels produced from a mixture of tetraethoxysilane (TEOS) and octyltriethoxysilane (OtEOS) both with and without immobilized Ru(II) *tris*(4,7-diphenyl-1,10-phenanthroline) dichloride as well as DSC and TG data for films deposited by deep- or spin-coating from the same gels, are reported. The initial products are characterized by elemental analysis, IR, solid state NMR and mass spectroscopy. Elemental analysis and IR spectroscopy are applied for identification of some of the intermediates obtained after heating at different temperatures. The final products are characterized by X-ray diffractometry. A hypothesis for the thermodecomposition processes taking place is proposed. The results reported contribute to elucidation of the properties as well as the temperature intervals in which the studied microcomposites could be used as sensing components of oxygen sensors.

Keywords. Ru(II) complexes; sol–gel technology; oxygen sensors; SiO_2-based matrix.

1. Introduction

The thermal decomposition of tetraethoxysilane (TEOS) in gas phase has been studied (Desu 1989; Van Der Vis *et al* 1993; Sataka *et al* 1994; Sirakami *et al* 1996) in absence and in presence of O2, water and other reagents as proposed by Van Der Vis *et al* (1993). The decomposition products have been revealed (Van Der Vis *et al* 1993; Sataka *et al* 1994) and the scheme of the processes taking place has been proposed (Sirakami *et al* 1996; Davazoglou and Vamvakas 1999). Kamiya *et al* (1990) studied the decomposition of gels based on triethoxymethylsilane (MtEOS) in different media. In a series of papers from Zaharescu and co-workers (Zaharescu *et al* 1999, 2001, 2003), the composition and thermal stability of SiO_2-based inorganic–organic hybrid materials produced from different types of organically modified silicates (ormosils) as precursors have been investigated. Furthermore, they have studied the influence of hydrocarbon radical's nature, solvent and water content in the initial solution on the gelation process as well as thermal stability in comparison with the behaviour of gels produced from TEOS. They also have discussed a hypothesis proposed for the chemistry of the processes taking place. Structural and thermochemical investigations of TEOS–tetraethoxytitanate–ormosils based hybrids used for obtaining corrosion protective coatings have been carried out based on earlier studies (Que *et al* 2000; Nocun *et al* 2005). The MtEOS, triethoxyvinylsilane, trimethoxymethylsilane (Zaharescu *et al* 2001, 2003; Nocun *et al* 2005) and 3-glicidoxypropyltrimethoxysilane studied by Nocun *et al* (2005) have been used both solely and in mixtures as precursors.

SiO_2-based inorganic–organic hybrid layers have been used as immobilization matrix for photoactive dyes, forming O_2 sensing devices (McDonagh *et al* 1998; Sang-Kyung Lee *et al* 2001). Ru(II)*tris*(4,7-diphenyl-1,10-phenanthroline) dichloride (Hyung *et al* 2006), the photoluminescence of which depends on the oxygen content in the medium, has most often been used as an active material. TEOS and ormosils-type precursors have been the starting materials for matrix production (McDonagh and MacCraith 1998; Campbell and Uttamchandani 2004). It is believed that the presence of a longer hydrocarbon chain in the precursor ensures higher hydrophobic capacity of the matrix produced, thus, improving the device performance in liquid media (McDonagh *et al* 1998). The thermal stability of the matrix is one of the parameters defining the fields of application of the sensor. Murashkevich *et al* (2001) studied the heat treatment behaviour of alkoxy-derived hydrogels produced from TEOS with immobilized optically active bromcresol purple. The immobilization has been carried out by immersing a monolithic matrix in the indicator solution. There is no data in the literature available on the thermochemical behaviour of gels produced from ormosils-type precursors with long hydrocarbon chain.

The present paper deals with thermal decomposition of an inorganic–organic hybrid matrix produced both from

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TEOS and from a mixture of TEOS and octyl–triethoxysilane (OtEOS) without and with immobilized Ru(II) complex. The introduction of the complex is done by adding its solution to the initial TEOS–OtEOS sol.

2. Experimental

2.1 *Materials preparation*

The materials were prepared following a two-step process.

(i) The TEOS and OtEOS for the preparation of gels were obtained from Merck. The precursor was added to ethanol–water solution in such an amount to keep the mole ratio TEOS : ethanol : water = 1 : 4 : 16 and TEOS : OtEOS : ethanol : water = 1 : 1 : 4 : 16. In order to keep a value of pH = 1, a solution of 1 M HCl was added. The sol was magnetically stirred for 1 h at ambient temperature and after that aged for 18 h at 70°C. The Ru(II) containing gel was prepared by adding ethanol solution of Ru(II)*tris* (4,7-diphenyl-1,10-phenanthroline) dichloride (Rudpp, supplied by Alfa Aesar) in such an amount that a concentration of 2·5 g complex/dm3 sol was reached.

(ii) Films were deposited on microscopic glass plates from the above described gels, by dip coating using the device described by Dushkin *et al* (2006) at 0·4 mm/s dipping rate and 1–9 immersions as well as by the spin coating method (Spin coater Model KW-4A, USA) at 3000 rpm spinning rate, 20 s time of spinning.

2.2 *Thermal and structural characterization*

The differential scanning calorimetry study of the deposited films was carried out by DSC DuPont 910 classical flux type calorimeter in the temperature range 70–700°C. TG curves of the same samples were recorded by means of TA SDT Q600 thermogravimeter in static air at a heating rate of 20°C/min.

DTA, TG and DTG curves of the gels were taken by a derivatograph Paulic–Paulic–Erdey (MOM, Hungary). A mass of 0·500 g of the sample was heated up to either 600 or 1000°C in a synthetic corundum crucible with a heating rate of 10°C/min in static air with α-Al_2O_3 as reference. Some samples were heated to intermediate temperatures and the residues were treated by elemental analysis, IR spectroscopy and X-ray diffractometry.

The contents of H, C and N were determined by CHNOS Elemental Analyser (Hanau, Germany). IR spectra were taken by Nicolet Avatar 360 (resolution 2–4 cm^{-1}) using KBr as matrix. The X-ray diffraction patterns of the residues after heating to 600 and 1000°C for 4 h were taken by a powder diffractometer (Siemens D 500 using CuKα radiation filtered by secondary monochromator, 40 kV, 30 mA, 0·05 deg 2Θ scanning rate). Solid state ^{13}C and ^{29}Si NMR spectra of the as prepared gels were recorded at ambient temperature on a Bruker 250 WM (67 MHz). The mass spectra of the same gels were recorded on a JEOL JMS D 300 double focusing mass spectrometer coupled to a JMA 2000 data system. The compounds were introduced via a direct inlet probe, heated from 50–400°C at a rate of 100°/min. The ionization current was 300 mA, the accelerating voltage, 3 kV and the chamber temperature, 150°C.

3. Results and discussion

3.1 *Composition and some spectral characteristics of initial gels*

The relative content of C, H and N (in Ru-containing samples) in the gels along with their mass, IR, ^{29}Si and ^{13}C solid state NMR spectra are given in table 1, figures 1–4 and table 2, respectively. These data are not sufficient for a precise description of the composition, the molecular structure of all the species and constituents of the gels, but are sufficient for a grounded hypothesis of the thermochemical process to be proposed.

3.1a *Ru-free gels*: (i) *TEOS-produced gel*: Cyclic tetramers of the type, $C_2H_5OSi_4O_x(OH)_y{\cdot}H_2O$, seems to be the main part of the gel. Supposing $x = y = 5$ (figure 5a), the molar mass will be 340, a value above the maximal mass seen on the mass-spectrum (figure 1). It can be supposed that a condensation process, taking place in the course of analysis is in charge for the registered mass of 308. The contents of H and C calculated in such a form are 3·56% and 7·06%, respectively. The significant difference with the experimental values found (table 1) suggests that the formula proposed can be considered as a tentative one, only. The lower H-content found may also be ascribed to some drying of the gel before elemental analysis (no special precautions were taken for preservation of the water content in the samples).

Some spectroscopic data support qualitatively the formula proposed:

- The presence of water is proved by the bands in IR spectrum at 1650 cm^{-1} and around 3400 cm^{-1} (figure 2A (1)). The peak at 307–18 = 289 *u* (*u*, unified atomic mass unit) in the mass-spectrum (figure 1) most probably is due to the presence of water.
- The OH groups contribute to the 3400 cm^{-1} band (figure 2A (1)). The deprotonation of such a group could explain the 308–1 = 307 *u* peak in the mass spectrum (figure 1).
- The bands at 1088 cm^{-1} for ν_{as}(Si–O–Si) from tetramers and 460 cm^{-1} for δ(Si–O–Si) (Zaharescu *et al* 1999, 2003) for IR spectrum (figure 2A (1)) prove the condensation of the gel at 70°C and support the formula proposed.
- The band for ν_{as}(Si–O–Si) usually appearing at 1220 cm^{-1} proposed by Zaharescu *et al* (1999) is observed at 1188 cm^{-1} (figure 2A (1)). The shift can be ex-

Table 1. Content of H, C and N in the residues after heating (10°C/min) of the gels, produced from TEOS and TEOS + OtEOS.

Precursor	TEOS					TEOS + OtEOS			
	Ru-free		Ru-containing			Ru-free		Ru-containing	
Heating temperature (°C)	H	C	H	C	N	H	C	H	C
Initial	2·60	5·67	3·89	6·00	0·18	7·16	36·61	6·82	36·36
210	2·27	0·48	1·35	1·47	0·25	6·66	34·33	6·34	34·02
260	2·07	0·17	1·73	2·78	0·27				
300	2·02	0·11	1·73	3·39	0·24	5·85	30·28	5·75	32·77
400	1·86	0·44	1·19	1·79	0·25				
500	1·39	0·40	0·82	0·67	0·07	2·41	6·01	1·54	4·38
600	0·55	0·00	0·35	0·89	0·26	1·76	4·77	0·96	4·23
1000	0·30	0·00	0·09	0·65	0·004	0·12	1·22	0·06	1·83

Table 2. Shifts in solid state NMR spectra and peaks in mass spectra of the gels studied.

	Gel type			
	Ru-free		Ru-containing	
Technique used	TEOS	TEOS + OtEOS	TEOS	TEOS + OtEOS
^{28}Si NMR (ppm)	58·5, 90·9, 100·6, 111·9	64·5, 100·5, 108·7, 131·0		
^{13}C NMR (ppm)	61·4, 58·8, 17·4	59·2, 32·4, 29·8, 23·0, 18·0, 12·5	149·6, 135·8, 129·7; 61·1, 58·8, 17·4	124·6, 59·9, 32·4, 29·8, 23·0, 17·8, 14·2
Mass spectra* (*u*)	308 vw; 307 s, 289 m, 273, 243, 226, 183 vw; 168, 165 w; 155 m; 154, 136 vs; 124 m; 107 s; 90 m; 89,77 s; 63 m	460 m; 443, 329 vw; 309 w; 307, 289 vs; 242, 226, 182, 178 m; 165 s	613, 577, 523, 460, 397, 369, 313 vw; 307, 289 vs; 242, 189, 178 m; others	613, 460, 329 vw; 307, 289 vs; others

*vw, very weak; w, weak; m, middle; s, strong, vs, very strong.

plained by the superposition with Si–O(C) absorption band at 1150 cm^{-1} due to the presence of non-hydrolyzed TEOS-fragment. As a matter of fact, its presence is definitely proven by the carbon content in the gel (table 1).

- The presence of three types of Si-atoms is seen in the ^{29}Si NMR spectrum (figure 3). According to Sugahara *et al* (1997), the shifts at 90–91 ppm are due to $[(HO)_2SiO]_4$ and $(HO)_3SiO(HO)_2SiOSi(OH)_3$. Following the above proposed formula, the shift as seen in figure 3 could be ascribed to $HOSiO_3$, $(HO)_2SiO_2$ and $HOSiO_2OC_2H_5$ bonded in cyclic tetramers.
- The shift at 17 ppm in the ^{13}C NMR spectrum (figure 4) may be ascribed to CH_3. The doublet at 58–61 ppm should be related to CH_2–O–Si.

(ii) *TEOS + OtEOS-produced gel*: The mass spectra (and more specifically, the presence of a peak at 307 *u* (table 2)) suggests some similarity in the composition of TEOS and TEOS + OtEOS produced gels. The formula shown in figure 5b is proposed by analogy to the one describing pure TEOS gel (figure 5a). It is confirmed by the satisfactory coincidence between the experimentally founded relative contents of H and C in the gel (table 1) and calculated ones according to the formula proposed (8·50% and 37·99%, respectively). Probably, species with only one C_8H_{17} group determines the mass peak at 460 *u* registered in the mass spectrum (figure 1).

- The presence of C_8H_{17} in the gel is confirmed by the IR bands at 696 (Si–CH_2), 1479 ($\delta(CH_2)$), 2885 (CH_2), 2976 (CH_3, CH_2CH_3), 2960 (CH_3) cm^{-1} (figure 2B (1)). They appear along the bands seen in the spectrum of the TEOS-produced gel (figure 2A (1)).
- As can be expected, the presence of C_8H_{17} leads to changes in ^{29}Si and ^{13}C NMR spectra compared to the ones with pure TEOS-produced gel (table 2).

3.1b *Ru-containing gels*: The peaks in the mass spectrum at 307 and 289 *u*, characteristics for the matrix, remain as most intensive in the mass spectra of the Ru-containing gels (table 2). The above mentioned peak at 307–18 = 289 *u* in the same spectrum confirms the presence of a relatively strongly bonded water molecule.

Due to rather small amount of Ru-complex, it has no any visible effect on the gel IR spectra (figures 2A (6), 2B (7)). These spectra preserve the pattern of the Ru-free ones (figures 2A (1), 2B (1)).

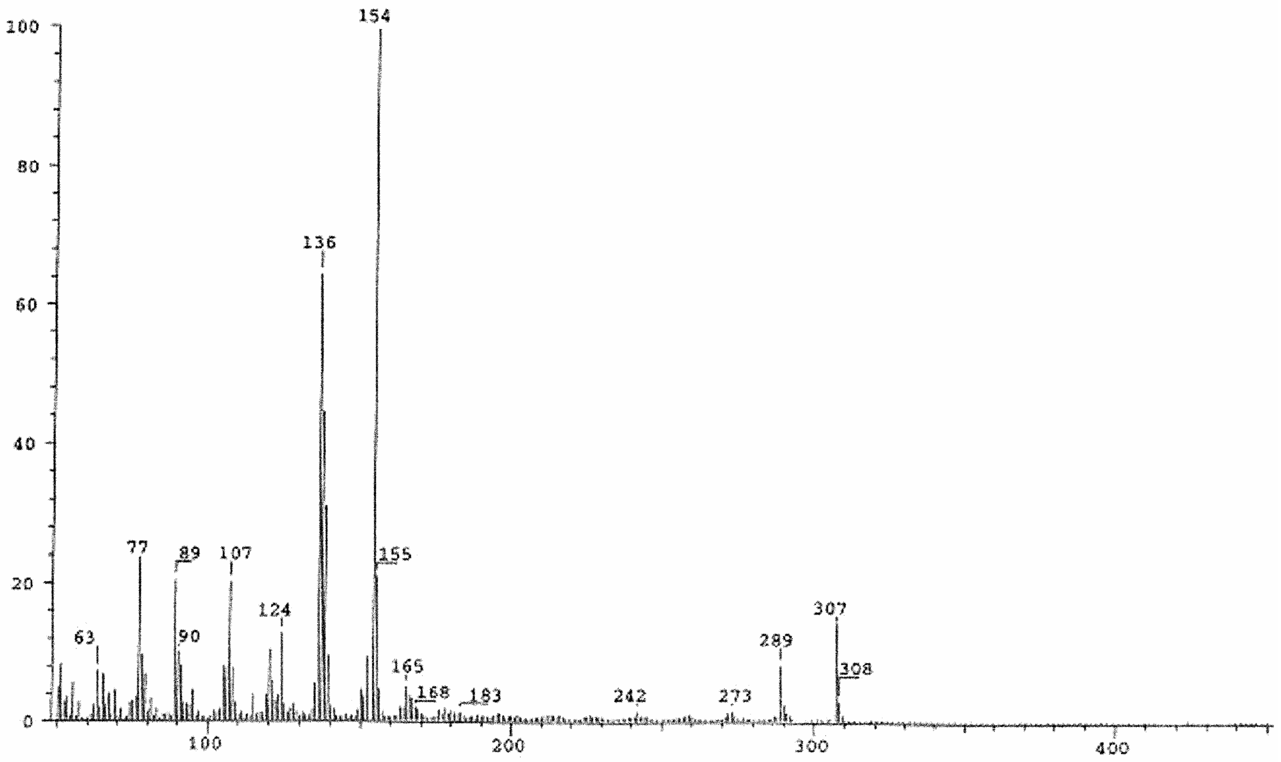

Figure 1. Mass spectrum of the initial Ru-free gel produced from TEOS.

However, the presence of complex influences the mass and NMR spectra (table 2). Masses of 613 *u* and higher in both the gel spectra are to be expected accounting for the complex molar mass of 1169·17 g/mol. The complex causes shifts between 130 and 149 ppm in ^{13}C NMR spectrum.

3.2 *Thermal decomposition*

DTA, DTG and TG curves of the gels are shown in figure 6. The quantitative data are summarized in table 3. DSC and TG curves, shown in figures 7 and 8, manifest the thermal behaviour of films, obtained from the respective gels (based on TEOS and TEOS + OtEOS precursors) coated by dip- and spin-techniques. The relative contents of H, C and N (in Ru containing samples) in intermediates heated to different temperatures are included in table 1.

3.2a *Ru-free gels*: (i) *TEOS-produced gel*: The TEOS gel is stable up to ~60°C (figure 6a). Endothermic process leading to sharp decrease of the mass (figure 6a, table 2, stage I) and of the relative content of carbon (table 1) takes place in the interval, 60–205°C. It has to be supposed that separation of ethanol resulted in the hydrolysis (mass loss, 13·5%) as well as slightly expressed condensation processes between two formula units, leading to evolving half a molecule of water per unit (mass loss, 2·6%) which are responsible for the process. The value of the thermal effect according to DSC results (figure 7) is not in contradiction to this supposition. These results are in agreement with the reported ones (Que *et al* 2000; Nocun *et al* 2005). The absorption band at 1188 cm^{-1} shifts to 1206 cm^{-1}. Figure 2A is the manifestation of the hydrolysis and decrease of the contribution of Si–O(C) vibration in this spectral area.

The relative content of hydrogen in the intermediate, obtained after heating to 210°C, is higher than the expected one (table 1). Most probably it is due to the hygroscopic nature of the intermediate and adsorption of atmospheric water in the time interval between heating and elemental analysis (no special precautions were taken to prevent such a process). The presence of water in the intermediate is also confirmed by the bands at 1650–1643 cm^{-1} and at around 3450 cm^{-1} (figure 2A (2)). The OH-groups (bonded to Si) which have not participated in the condensation process so far, contribute to the latter band.

A three-stage exothermic process takes place in the 205–525°C interval (figure 6a, table 2). It is attributed to progress of the polycondensation process. The decrease of the relative intensity of IR absorption band due to ν(Si–O/H/) at 950 cm^{-1} (figure 2A (4)) suggests that up to 500°C, the polycondensation is still in progress. The heating of the sample at higher temperatures decreases the residue's hygroscopic capacity and, consequently, leads to a decrease of H-content (table 1).

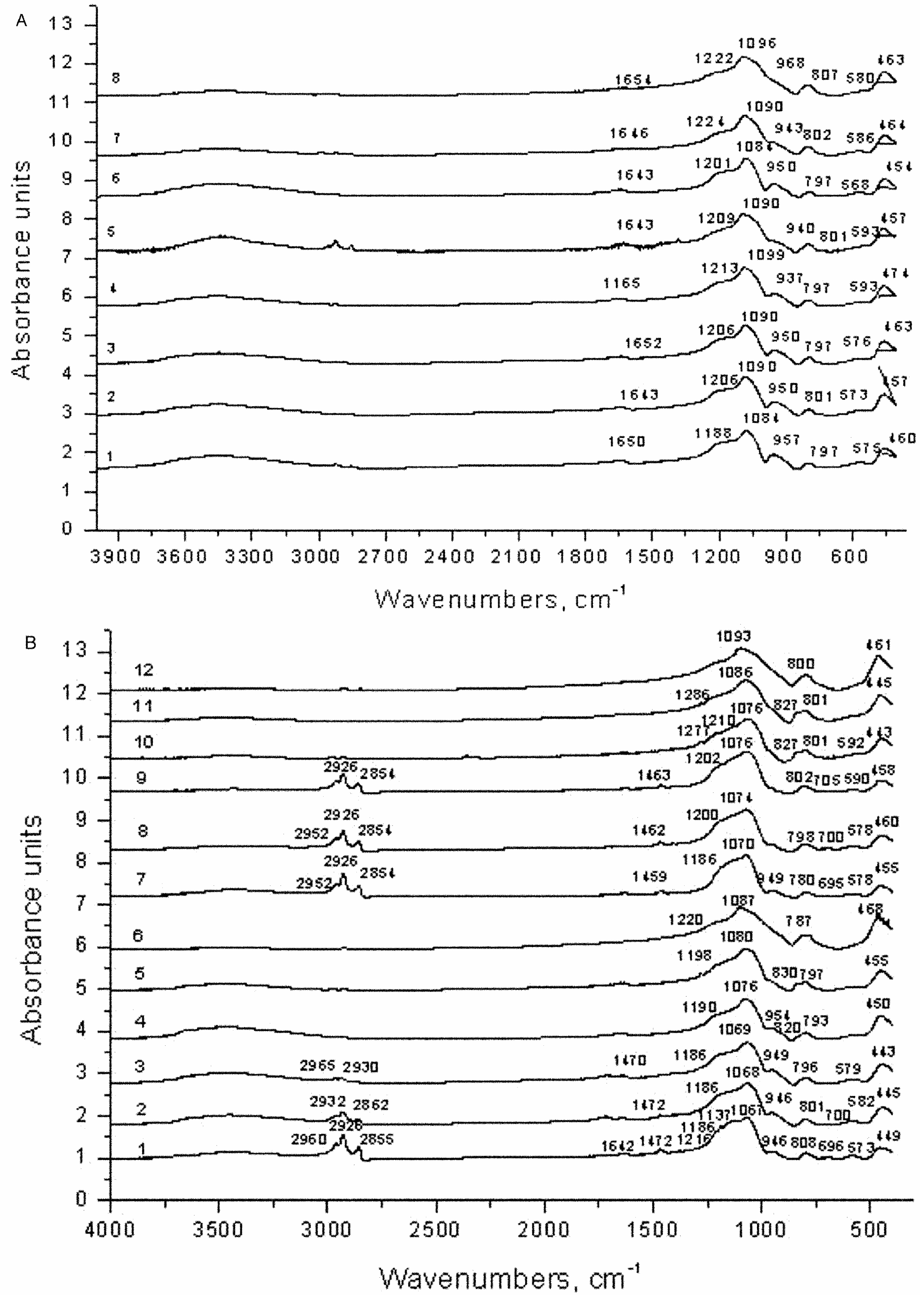

Figure 2. IR spectra (4000–400 cm^{-1}) of the initial gels and intermediates obtained after their heating: (A) produced from TEOS: Ru-free initial (1); intermediates heated to (°C): 210 (2), 300 (3), 500 (4), 600 (5); Ru-containing: initial (6); intermediates, heated to (°C): 300 (7), 500 (8) and (B) produced from TEOS + OtEOS: Ru-free: initial (1), intermediates heated to (°C): 210 (2), 300 (3), 500 (4), 600 (5), 1000 (6); Ru-containing: initial (7); intermediates heated to (°C): 210 (8), 300 (9), 500 (10), 600 (11), 1000 (12).

Table 3. Thermal decomposition of Ru-free and Ru-containing gels, produced from TEOS and TEOS + OtEOS.

Sample	Parameters (stages)	I	II	IIIa	IIIb	IV	V
TEOS	Temperature interval (°C)	20–205	205–260	260–480		480–525	525–600
	Δm/m* (%)	16·2	2·0	7·6		1·0	0·4
TEOS and Ru(II) complex	Temperature interval (°C)	20–240	240–270	270–360	360–420	420–500	500–600
	Δm/m* (%)	14·0	2·0	2·0	2·0	1·2	0·8
TEOS + OtEOS	Temperature interval (°C)	20–190	190–290	290–400	400–500	500–595	595–1000
	Δm/m* (%)	1·0	5·5	10·5	22·0	2·5	2·5
TEOS + OtEOS and Ru(II) complex	Temperature interval (°C)	20–200	200–310	310–420	420–485	485–620	620–1000
	Δm/m* (%)	1·5	5·0	11·0	17·5	5·0	2·0

*Relative decrease of the mass.

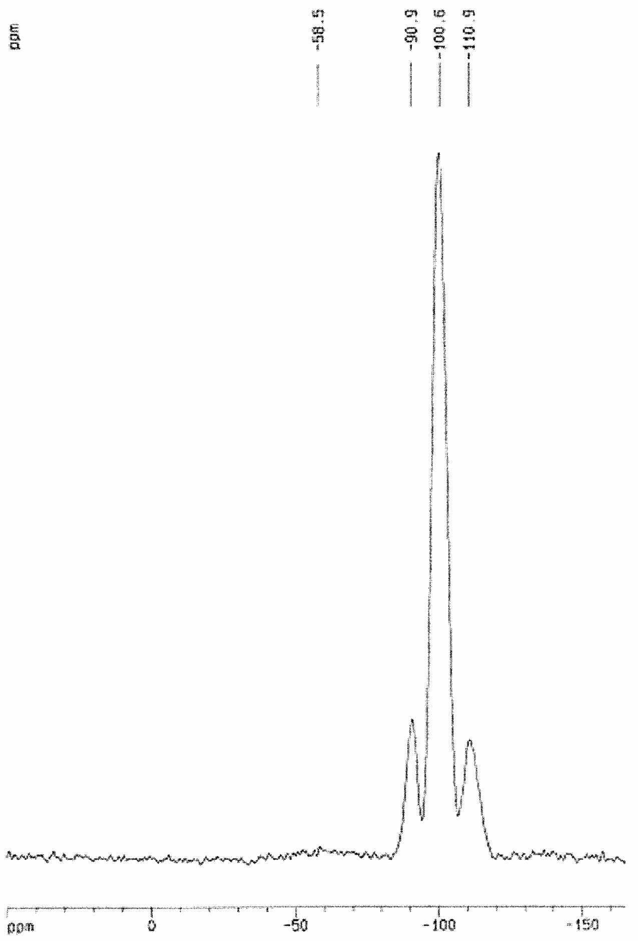

Figure 3. ^{29}Si NMR spectrum of the initial Ru-free gel produced from TEOS.

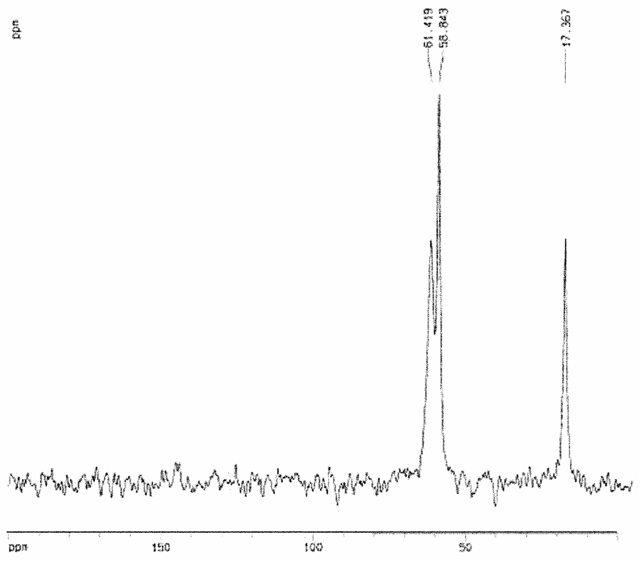

Figure 4. ^{13}C NMR solid state spectrum of the initial Ru-free gel produced from TEOS.

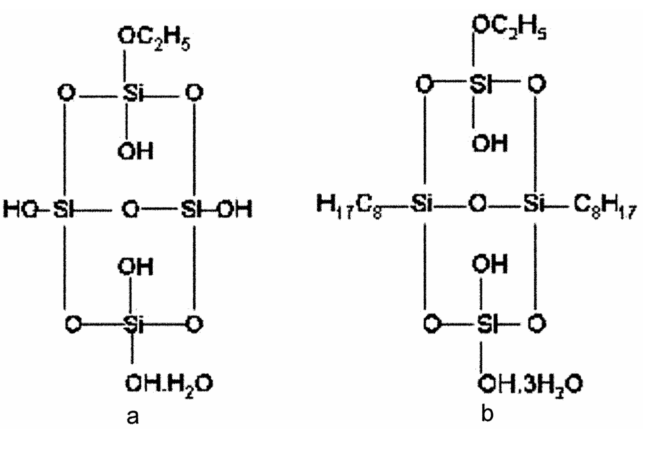

Figure 5. Supposed units formulae of the gels produced from TEOS (a) and TEOS + OtEOS (b).

The traces of carbon which remained in the residue (black in colour) burn just at about 600°C (table 1), probably causing the exoeffect seen in figure 7. Similar traces of carbon were found in metal–organic complexes heated up to the same temperature (Todorovsky *et al* 2002). The overall mass loss up to 600°C (27·2%) suggests the formation of a silicate net with a $Si_4O_5OHO_{5/2}$ unit (mass loss calculated at 26·8%). The residues heated at 600°C and 1000°C (for 4 h) are X-ray amorphous which is in good agreement with the earlier studies by Pol *et al* (2004) and Milanova and Todorovsky (1994).

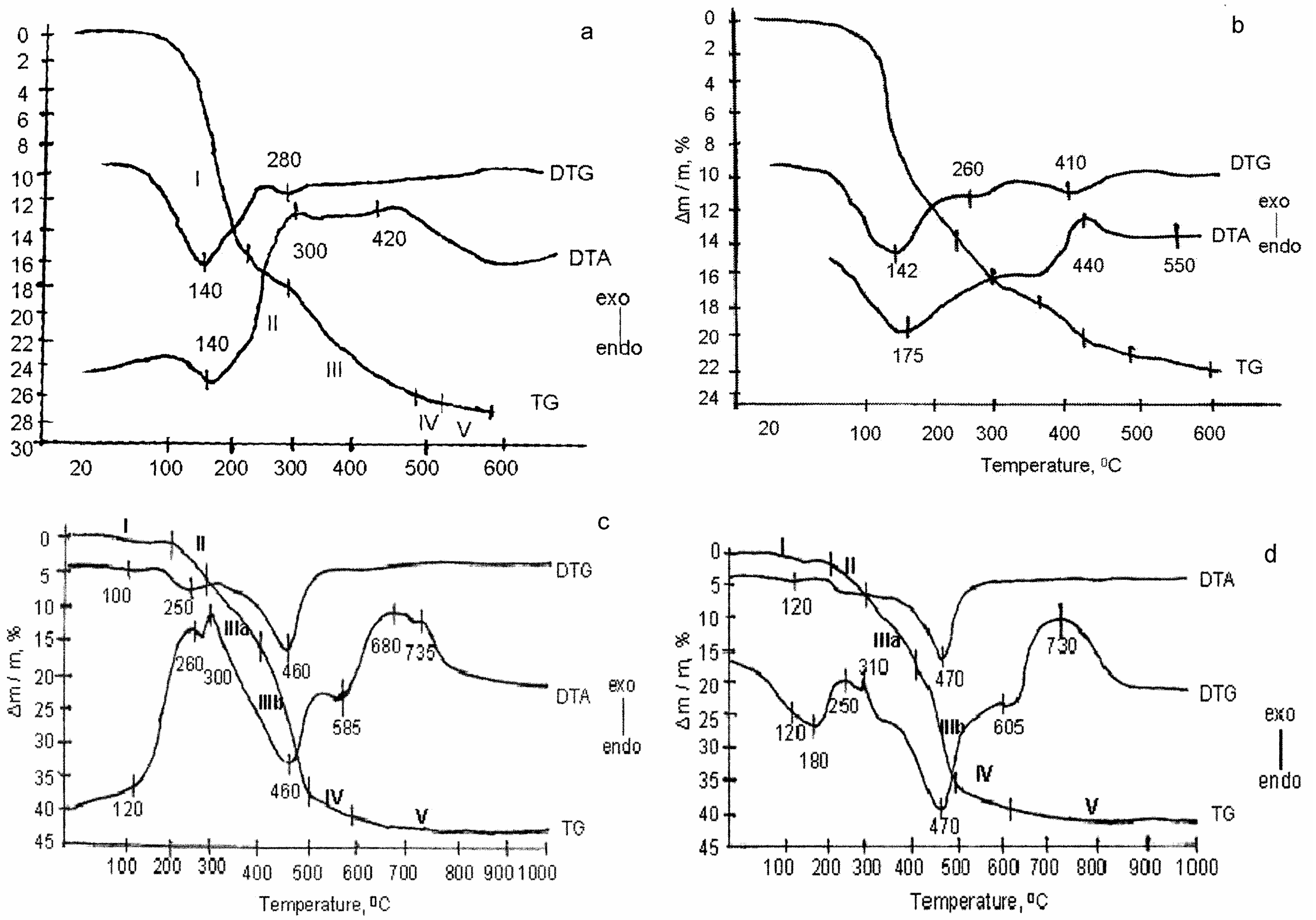

Figure 6. DTG, DTA and TG curves of the gels prepared from TEOS (**a**), TEOS + OtEOS (**c**) and the same with *Rudpp* (**b**, **d**). The number of the decomposition process stages are shown (see table 1).

The particles of <1 μm up to 2–3 μm in size disposed off on the glass-like material were observed in the sample heated at 600°C (figure 9a). The difference in the values of the Si-content in the material and of the particles is within the error limit of the method used (energy dispersive X-ray microanalysis). A layer structure (figure 9c) is revealed after heating up to 1000°C.

(ii) *TEOS + OtEOS produced gel*: The gel is thermally rather more stable than the one produced from TEOS only. Heating up to 190°C leads to mass loss of ~1% only. The mass loss in the following stage (190–290°C) may be ascribed to hydrolysis. The burning of the ethyl decomposition products caused the observed exoeffect. The relative decrease in the contents of C and H (table 1) is consistent with this supposition. The intensity of the band at 946 cm^{-1} (belonging to Si–OH) decreases so only a shoulder appears in the spectrum of the intermediate heated to 300°C (figure 2B (2)). The burning of C_8H_{17} proceeds step-wise between 300°C and 500°C leading to a sharp decrease of the C and H contents and a strong exoeffect. The bands at 2960–2855 cm^{-1} belonging to CH_2 and CH_3, as well as those at 1472 cm^{-1} ($\delta(CH_2)$) and at 696 cm^{-1} (Si–CH_2) disappear (figure 2B (10)). The destruction of the organic components of ormosils type precursors has also been found in the same temperature interval by other researchers (Zaharescu *et al* 1999, 2003; Que *et al* 2000; Nocun *et al* 2005) depending on the type of organic component and on the ratio between TEOS and ormosil-precursor. When heating was performed in inert atmosphere, the Si–CH_3 bond disrupts at 700–800°C. The step wise thermal destruction of ethyl–hexyl radicals is found by Milanova and Todorovsky (1994). The burning of carbon that remained (in charge for the black colour sample) proceeded in a few stages above 500°C. After heating to 600°C, the black colour of the intermediate and significant carbon content (table 1) are still preserved. The sample is X-ray amorphous. The H content decreases (table 1) as a result of condensation and Si–OH band disappears (figure 2B (11)). The exoeffects around 680°C and 735°C (figure 6c) are probably related to the burning of carbon. As can be expected in thin films this effect is observed at lower temperature (~600°C). Bands belonging to Si–O–Si polymers only appear in the

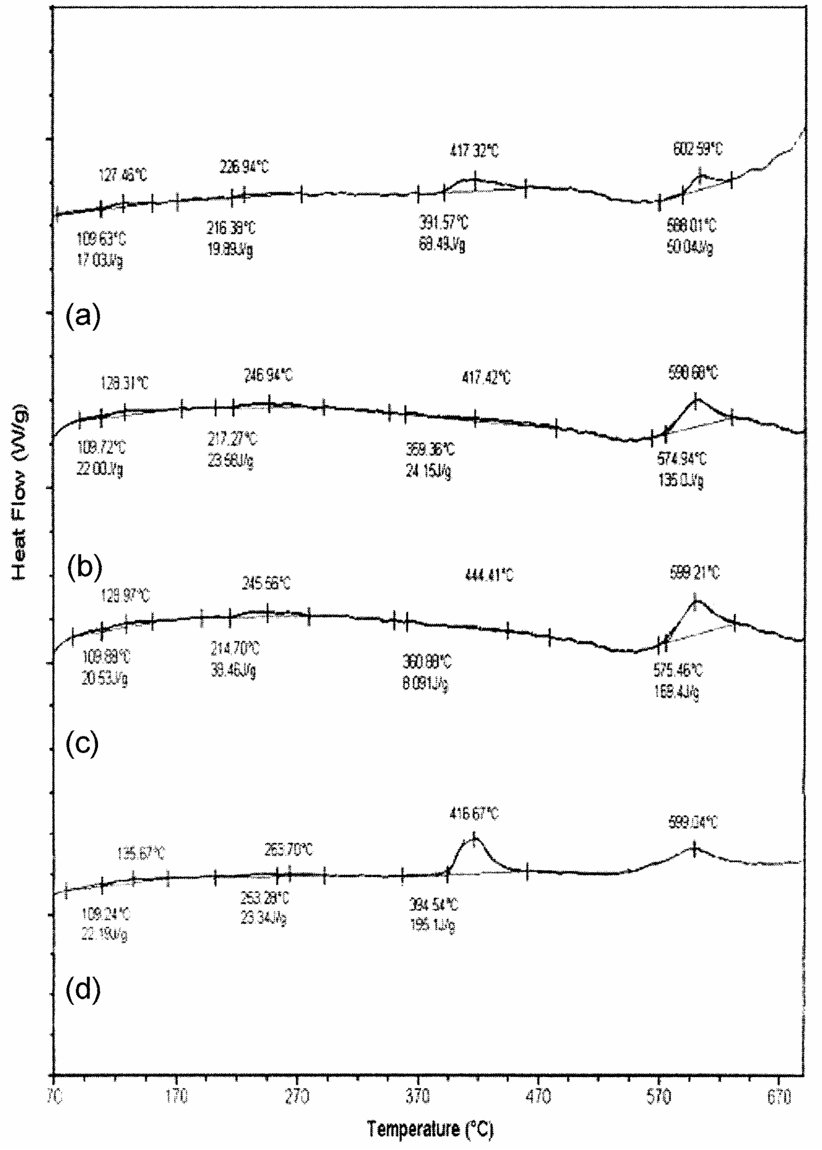

Figure 7. Thermal curves of thin films deposited by dip coating technique (1 immersion): (a) TEOS + OtEOS and *Rudpp*, (b) TEOS and *Rudpp*, (c) TEOS + OtEOS and (d) spin coating technique (20 s, 3000 rpm) from TEOS + OtEOS and *Rudpp*.

IR spectrum of the final product (figure 2B (12)). No changes in crystallinity and colour are observed after heating for 4 h to 1000°C in spite of carbon burning.

3.2b *Ru(II)-containing gels and films*: (i) *TEOS-produced gel*: The DTA curve of the Ru-containing TEOS-produced gel (figure 6b) shows some differences compared with the one of Ru-free gel.

The endothermic process (figure 6b) of C_2H_5OH evolution is analogous to the one observed in Ru-free gel but takes place at a little higher temperature, probably in two steps, up to 240–250°C. Up to ~270°C, the small mass loss is not accompanied by a significant thermal effect. Most probably at this temperature the complex undergoes some transformation accompanied with clearly seen deepening of the colour but not with a significant decrease of the N-content in the gel (table 1). The increase of the carbon relative content in the intermediates obtained after heating to 260°C and 300°C (table 1) suggests that the polycondensation process starts below 260°C. The decrease of the 943 cm^{-1} IR band relative intensity (due to ν(Si–O(H)) observed in the spectrum of the sample heated to 300°C (figure 2A (7)) confirms this supposition. No significant differences with the thermochemical behaviour of the analogous Ru-free sample are observed (table 3).

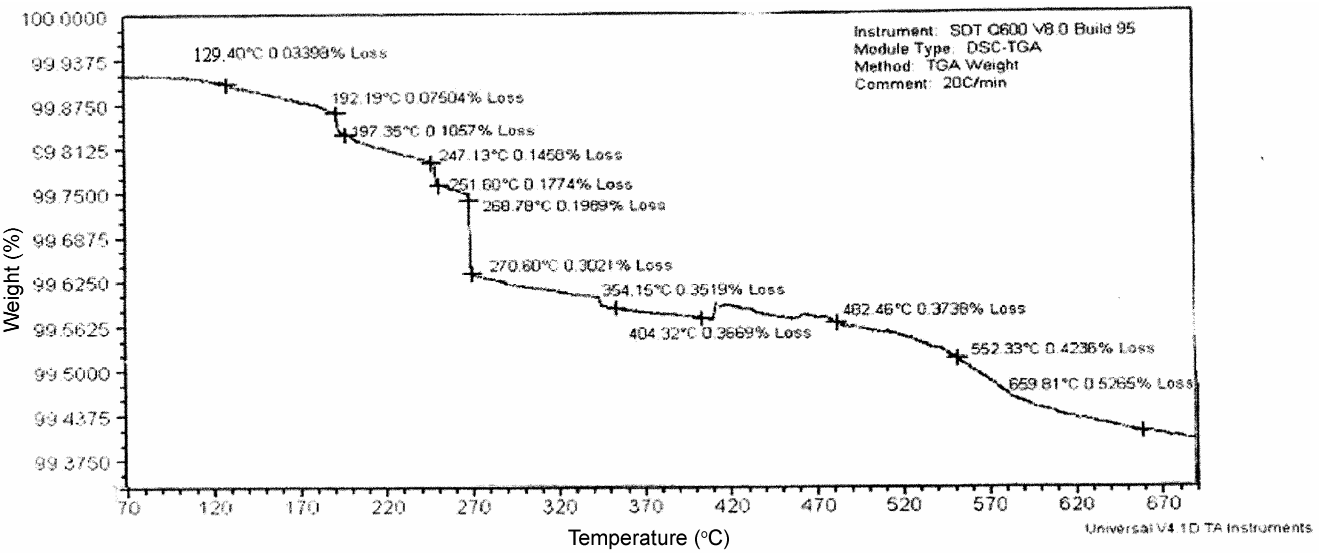

Figure 8. TG curve of the film produced by dip-coating from TEOS + OtEOS and *Rudpp* (9 immersions).

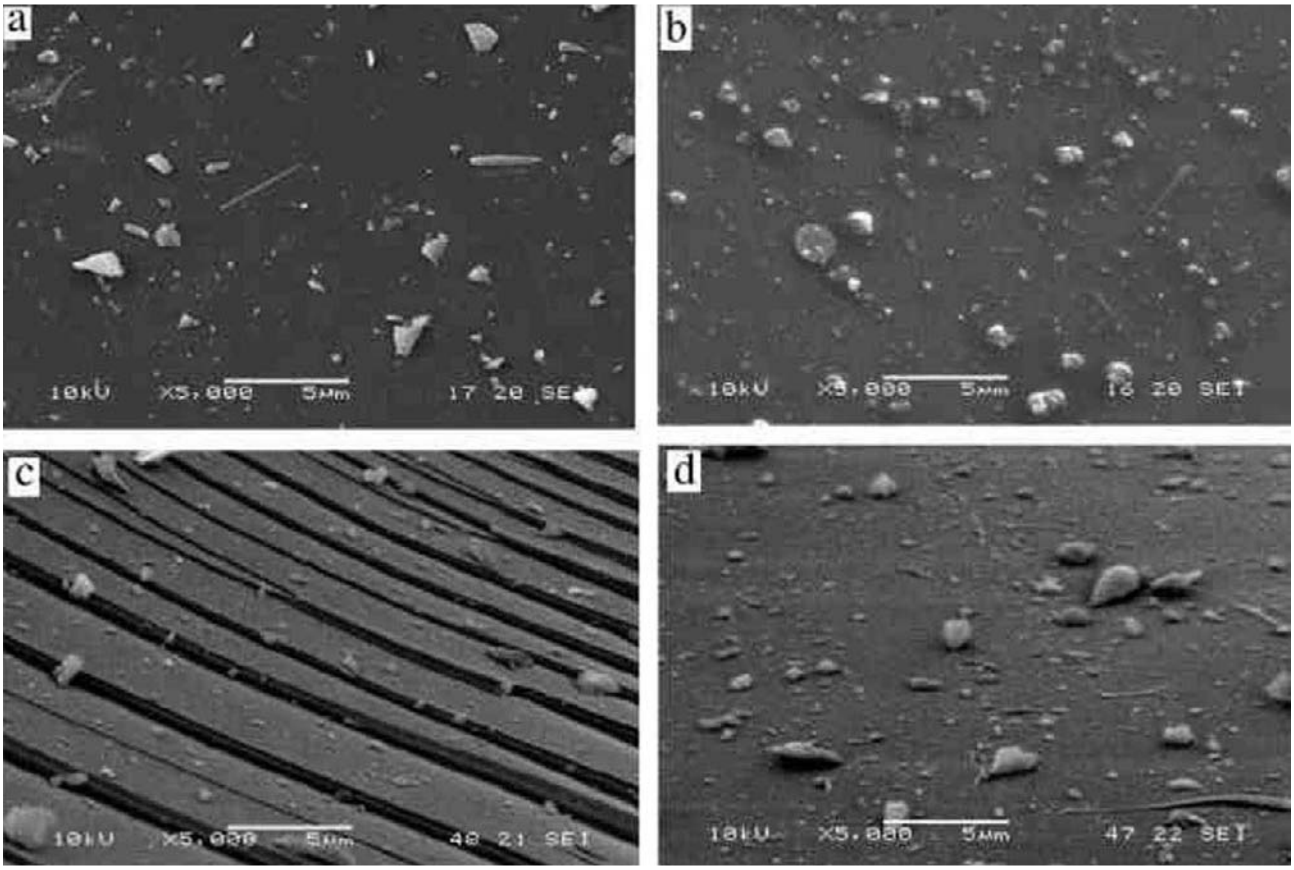

Figure 9. SEM images (× 5000) of residues after heating to 600°C (**a**, **b**) and to 1000°C (**c**, **d**) of gels prepared from TEOS (**a**, **c**) and the same with immobilized *Rudpp* (**b**, **d**).

Probably the destroying of the Ru-complex contributes to the DTG and DTA effects at 410°C and 440°C, respectively (figure 6b).

The polycondensation process proceeds and the 943 cm^{-1} band in the IR spectrum of the intermediate obtained at 500°C (figure 2A (8)) appears as a shoulder.

The sharp decrease of the nitrogen content (table 1) proves the full destruction of the complex above 400°C. The exoeffect appearing around 550°C in the gel (figure 6b) and at 600°C in the respective film (figure 7c) has to be attributed to burning of the carbon.

(ii) *TEOS + OtEOS-produced gel*: No principle differences in the DTG, DTA and TG (figures 6c, d; table 3) and DSC (figures 7a, c) curves are caused by the presence of Ru-complex in the gel.

The stages of the process are very well expressed on the TG-curve of the relatively thicker ormosil type film (figure 8). The decrease of the relative contents of C and H in the course of heating is similar to that of the analogous Ru-free complex. It may be supposed that the Ru-complex destruction contributes significantly to the exoeffect at 417°C seen on the DSC curve of the film (figure 7d).

No significant differences are observed in DSC (figure 7d) and TG-behaviour of the film deposited by spin instead of dip coating.

The SEM image (figure 9d) is rather different compared with the Ru-free sample. It seems that the Ru suppressed the formation of the layer structure observed in the Ru-free sample.

4. Conclusions

The reported data permit to make hypothesis on the composition of the gels produced from TEOS and TEOS + OtEOS used as Si-precursors as well as on the processes taking place during their thermal decomposition. The data obtained could be useful for the evaluation of the region of temperatures in which the studied materials probably could work as oxygen sensors in air atmosphere.

Acknowledgements

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