

PYROLYSIS STUDY OF FLUORINATED SOL–GEL SILICA

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Abstract

Fluorinated silica gels at various fluorine content were prepared via sol-gel by hydrolysis of 3,3,3-trifluoropropyltrimethoxysilane and tetraethoxysilane mixtures. The gels, of nominal stoichiometry $\text{Si}(\text{CH}_2\text{CH}_2\text{CF}_3)_x\text{O}_{(2-x/2)}$ ($x=0.1-1$), were characterized by FT-IR, X-ray photoelectron spectroscopy (XPS) and N_2 adsorption analysis. The thermal stability of the fluorinated samples was investigated by coupling thermogravimetric measurements with mass spectrometric and gas chromatographic analyses of the evolved gaseous species. The chemical reactions occurring in the gel matrices during heating were siloxane chain rearrangements involving condensation between residual hydroxyl and ethoxyl groups in the 100–350°C temperature range, whereas the thermal decomposition of the fluoroalkyl groups were observed at higher temperatures (450–600°C). The release of the fluoroalkyl moieties also involved C–F/Si–O bond exchanges inside the siloxane chains, with gas-phase evolution of different fluorinated silicon units.

Keywords: fluorinated silica gels, pyrolysis study, sol–gel synthesis, thermogravimetric-mass spectrometric-gas chromatographic coupled analyses

Introduction

Among the various species used to improve the physical properties of silica glasses, fluorine is very attractive since its incorporation reduces the refractive index without optical absorption in the transmission region due to the substitution of non-bridging oxygen with $\equiv\text{Si}-\text{F}$ bonds [1–3]. Usually, fluorine doping for optical fibre fabrication is obtained by means of suitable vapour deposition techniques starting from precursors such as SF_6 , SiF_4 , CF_4 , C_2F_6 and HF [4, 5]. In this study, silica based materials have been synthesized by adopting the sol-gel route as an alternative process. To this aim the attention was first focused on the preparation of silicon oxyfluoride gels by hydrolysis-condensation of triethoxyfluorosilane under different conditions. Unfortunately, the monolithic and transparent silicon oxyfluoride matrices, of nominal composition $\text{SiO}_{(2-0.5x)}\text{F}_x$ ($x \leq 0.52$), resulted morphologically and chemically unsta-

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ble when stored in air [6]. Consequently, the hydrolysis of a silicon precursor modified with an alkylfluorinated group was studied in order to prepare stable fluorine doped silica materials and suitable for technological employment.

In this work we report the synthesis and thermal characterization of monolithic and transparent gels, obtained from solutions of $\text{CF}_3\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ and $\text{Si}(\text{OEt})_4$ in different molar ratios. In particular, the chemical composition of the samples was investigated by XPS whereas the thermal stability was studied by coupling thermogravimetric analysis (TG) with gas-chromatographic (GC) and mass spectrometric measurements (MS) of the evolved gas species.

Experimental

Chemicals

3,3,3-Trifluoropropyltrimethoxysilane (purchased from ABCR) and tetraethoxysilane (Aldrich) were pure reagents, used without any further purification. HCl (1 M) and NH_3 (10^{-3} M) solutions were obtained by dilution of Carlo Erba pure reagents (HCl 37%, $d=1.186 \text{ g cm}^{-3}$; NH_3 31.75%, $d=0.89 \text{ g cm}^{-3}$).

Instrumentation

FT-IR spectra were recorded on a Nicolet 5 DXC Fourier-transform infrared spectrometer in the $400\text{--}4000 \text{ cm}^{-1}$ range on KBr pellets, working in transmission mode and averaging 64 scans.

Specific surface areas and pore size values were determined by N_2 adsorption at 77 K, carried out on an ASAP 2010 Micromeritics analyzer. Equilibrium points were considered inside the $0.05\text{--}0.33 \text{ p/p}^\circ$ range; data were processed by B.E.T. and B.J.H. equations [7, 8].

XPS analyses were performed with a Perkin Elmer Φ 5600-ci spectrometer using non-monochromatized AlK_{α} radiation (1486.6 eV). Ground samples, analysed as pellets, were directly introduced by a fast-entry lock system into the XPS analytical chamber. The working pressure was $<5 \cdot 10^{-8}$ Pa. The spectrometer was calibrated assuming the binding energy (BE) of the Au $4f_{7/2}$ line at 83.9 eV with respect to the Fermi level. The standard deviation for the BE values was 0.2 eV. The reported BE's were corrected for charge effects, assigning the BE value of 284.8 eV to the C1s line of adventitious carbon [9]. Survey scans were run in the $0\text{--}1350$ eV range. Detailed scans were recorded for the Si2p, C1s, O1s and F1s regions. The analyses involved Shirley-type background subtraction and non-linear least-squares curve fitting, adopting Gaussian-Lorentzian peak shapes and peak area determination by integration. The atomic compositions were evaluated by using sensitivity factors supplied by the spectrometer manufacturer, taking into account the geometric configuration of the apparatus.

Thermogravimetric (TG) and differential thermal analyses (DTA) were performed on a LabSys Setaram thermobalance operating in the $20\text{--}1000^\circ\text{C}$ range, with

a heating rate of $10^{\circ}\text{C min}^{-1}$, under $100\text{ cm}^3\text{ min}^{-1}$ He flux. Powdered gels were analysed using alumina crucibles and $\alpha\text{-Al}_2\text{O}_3$ as reference.

Gas chromatographic (GC) analysis were carried out on an HRGC Carlo Erba Instruments chromatograph, equipped with a GR8 Bimatic thermostatted micro-valve for gas sampling, and a VG-QMD-1000 Carlo Erba Instruments quadrupole mass spectrometer as detector. Chromatographic elutions were performed by using a PoraPlot Q Chrompack (25 m, 0.32 mm) capillary column with a temperature program of 30°C for 5 min, followed by $5^{\circ}\text{C min}^{-1}$ heating rate up to 200°C , held for 15 min. Helium was used as carrier gas with 15 kPa inlet pressure.

Electron impact mass spectra (70 eV) were continuously registered and stored with frequency 1 scan s^{-1} ranging from 2 to 500 amu.

The instrumental interfaces, experimental procedure and data processing adopted in the pyrolysis study of the gels, based on the coupled thermogravimetric-mass spectrometric (TG-MS) and thermogravimetric-gas chromatographic-mass spectrometric (TG-GC-MS) measurements, are described elsewhere [10–15].

Results and discussion

Synthesis of gel-samples

Several attempts were made to gel the pure $\text{CF}_3\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ precursor by hydrolysis-condensation under various conditions, i.e. different $\text{H}_2\text{O}/\text{Si-OR}$ and solvent/Si-precursor molar ratios, acidic catalysts and temperature processing. A nearly homogeneous gel was only obtained by adding dropwise, under vigorous stirring, an appropriate volume of a 10^{-3} M NH_3 solution to the pure 3,3,3-trifluoropropyltrimethoxysilane. In this case, the initial emulsion turned to a quite opalescent solution after some hours, yielding a gel within one day, which was labelled as T^{RF} sample. Taking this into consideration, the synthesis of fluorinated gels with desired features was carried out by diluting the pure alkyl-modified precursor with the more reactive tetraethoxysilane. Mixtures of $\text{CF}_3\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ and $\text{Si}(\text{OCH}_2\text{CH}_3)_4$ of different molar ratios were easily hydrolyzed in absence of solvent, by adding dropwise appropriate volumes of a 1 M HCl solution, in order to satisfy the stoichiometric $\text{H}_2\text{O}/\text{Si-OR}=1$ ($R=\text{CH}_3, \text{CH}_2\text{CH}_3$) demand. The initial emulsions, kept under vigorous stirring and cooled by a water flux, turned into transparent solutions after 15–60 min, yielding colourless monolithic gels within 2–7 days. Table 1 summarizes the values of sol-gel parameters employed in the synthesis of the different samples. All the fluorinated gels were dried by aging the samples for two months at room temperature in air and then by a slowly reduced pressure treatment up to 0.1 hPa. The dried gels were labelled considering their nominal composition as $\text{Q}/\text{T}^{\text{RF}}=9/1, =7/3, =1/1, =3/7$ and $=1/9$, where Q and T^{RF} represent the poly-condensed silicon units inside the siloxane matrices, deriving from $\text{Si}(\text{OCH}_2\text{CH}_3)_4$ and $\text{CF}_3\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ precursors, respectively.

Table 1 Experimental parameter values employed in the synthesis of fluorinated gels obtained starting from $\text{CF}_3\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ and $\text{Si}(\text{OCH}_2\text{CH}_3)_4$ precursors

Sample	$\text{CF}_3\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ amount/g; mol	$\text{Si}(\text{OEt})_4$ amount/g; mol	Hydrolysing solution/ cm^3 ; moles of H_2O mol	Time of gelling/ days
Q	–	3.120 ; $1.50 \cdot 10^{-2}$	HCl $1 \text{ M}/1.1$; $6.00 \cdot 10^{-2}$	1
$\text{Q}/\text{T}^{\text{RF}}=9/1$	0.500 ; $2.29 \cdot 10^{-3}$	4.295 ; $2.06 \cdot 10^{-2}$	HCl $1 \text{ M}/1.6$; $8.93 \cdot 10^{-2}$	2
$\text{Q}/\text{T}^{\text{RF}}=7/3$	1.000 ; $4.58 \cdot 10^{-3}$	2.227 ; $1.07 \cdot 10^{-2}$	HCl $1 \text{ M}/1.0$; $5.65 \cdot 10^{-2}$	3
$\text{Q}/\text{T}^{\text{RF}}=1/1$	1.500 ; $6.87 \cdot 10^{-3}$	1.432 ; $6.87 \cdot 10^{-3}$	HCl $1 \text{ M}/0.9$; $4.81 \cdot 10^{-2}$	4
$\text{Q}/\text{T}^{\text{RF}}=3/7$	2.000 ; $9.16 \cdot 10^{-3}$	0.818 ; $3.93 \cdot 10^{-3}$	HCl $1 \text{ M}/0.8$; $4.32 \cdot 10^{-2}$	5
$\text{Q}/\text{T}^{\text{RF}}=1/9$	2.000 ; $9.16 \cdot 10^{-3}$	0.212 ; $1.02 \cdot 10^{-3}$	HCl $1 \text{ M}/0.6$; $3.16 \cdot 10^{-2}$	7
T^{RF}	3.000 ; $1.38 \cdot 10^{-2}$	–	NH_3 $10^{-3} \text{ M}/0.8$; $4.14 \cdot 10^{-2}$	1

Specific surface area and porosity determinations, FT-IR and XPS data

N₂ adsorption measurements show isotherm curves typical of a mesoporous material for the Q/T^{RF}=9/1 gel, and of macroporous networks for all the other samples. The data were processed by B.E.T. and B.J.H. equations and the obtained specific surface area and average pore diameter values are reported in Table 2. Such values for the samples annealed up to 1000°C and for a typical SiO₂-gel (Q sample) obtained by Si(OCH₂CH₃)₄ under the same conditions [16] are also reported for comparison. The use of the fluoroalkyl modified silicon precursor drastically decreases the specific surface area of the fluorinated silica matrices. As a matter of fact, 10% of T^{RF} presence is sufficient to reduce to less than 50% the area value, if compared to a gel made only of 'Q' silicon units. Except for Q/T^{RF}=9/1 gel, the surface areas of samples heated up to 1000°C present values slightly higher than the correspondent initial specimens. In conclusion, a different morphology is evidenced for the Q/T^{RF}=1/9 and T^{RF} samples taking into account their average pore diameter values.

The FT-IR spectrum of the pure T^{RF} gel shows an absorption pattern strictly correlated to the starting alkoxide precursor. In particular, the presence of the fluorinated propyl group gives rise to specific sharp peaks at 1452, 1379, 1321, 1271, 1223, 1024, 901, 839, 704 and 553 cm⁻¹ [17, 18] as shown in Fig. 1. The relative intensities of these signals progressively decrease in the spectra of gels obtained by increasing the amount of tetraethoxysilane in the starting alkoxide mixtures. Moreover, a progressive variation in the absorption of the Si-O-Si band was also observed in the gels as a function of the alkoxide molar percentages: the most intense band at 1129 cm⁻¹ and the sharp peak at 1070 cm⁻¹, observed in pure T^{RF} gel, changed to a strong band at 1080 and a weak shoulder at ca. 1215 cm⁻¹, typical of the pure silica gel [16, 19]. IR spectra of gels with compositions Q/T^{RF}<1/1 show a weak signal at ca. 3700 cm⁻¹ due to the presence of isolated ≡Si-OH groups, whereas the spectra of samples with higher content of silicon Q units present a more intense broad band at ca. 3400 cm⁻¹ attributable to hydrogen bonded hydroxy groups. The presence of ≡Si-OH groups inside the siloxane matrix is also strictly related to its specific surface area as shown by the morphological data summarized in Table 2. The IR signals due to silanol groups significantly decrease in the samples heated up to 400°C under inert atmosphere, whereas no relevant changes regarding the fluoroalkyl group presence are observed in these samples. On the other hand, the absorptions of the fluoroalkyl moiety are no more present in samples annealed over 600°C. Independently on the initial alkoxide mixture composition, the spectra of gels pyrolyzed up to 1000°C are quite similar; they present an intense asymmetric band at 1103 cm⁻¹ with a shoulder at ca. 1220 cm⁻¹, and two broad peaks at 800 and 460, typical of a SiO₂ matrix formed of totally condensed Q units. Finally, the spectra of mixed Q/T^{RF} gels heated at temperatures higher than 600°C show the presence of a weak signal at 931 cm⁻¹ which may be attributed to Si-F bonds [6].

XPS analysis was performed to characterize the chemical composition of the fluorinated silica gels as a function of the nominal Q/T^{RF} ratio and their subsequent thermal treatments. The composition data for all samples, given as atomic %, are re-

Table 2 Morphological characterization of fluorinated gels; N₂ adsorption data were evaluated by BET and BJH equations^a

Sample	Room temperature dried gels				Sample annealed up to 1000°C			
	Specific surface area/m ² g ⁻¹	Average pore diameter/nm	Total pore volume/cm ³ g ⁻¹	Total pore volume/cm ³ g ⁻¹	Specific surface area/m ² g ⁻¹	Average pore diameter/nm	Total pore volume/cm ³ g ⁻¹	Total pore volume/cm ³ g ⁻¹
Q	664.0	2.7	0.293	0.293	1.0	43	0.003	0.003
Q/T ^{RF} =9/1	314.0	3.9	0.136	0.136	7.0	29	0.033	0.033
Q/T ^{RF} =7/3	5.0	16.0	0.012	0.012	10.5	22	0.047	0.047
Q/T ^{RF} =1/1	2.4	45.7	0.009	0.009	7.4	28	0.039	0.039
Q/T ^{RF} =3/7	1.4	53.5	0.006	0.006	3.6	37	0.021	0.021
Q/T ^{RF} =1/9	3.0	6.6	0.003	0.003	b	b		
T ^{RF}	1.1	6.8	0.002	0.002	b	b		

^aReported data are affected by an average 5% uncertainty^bData not available for the tendency of the sample to sublimate

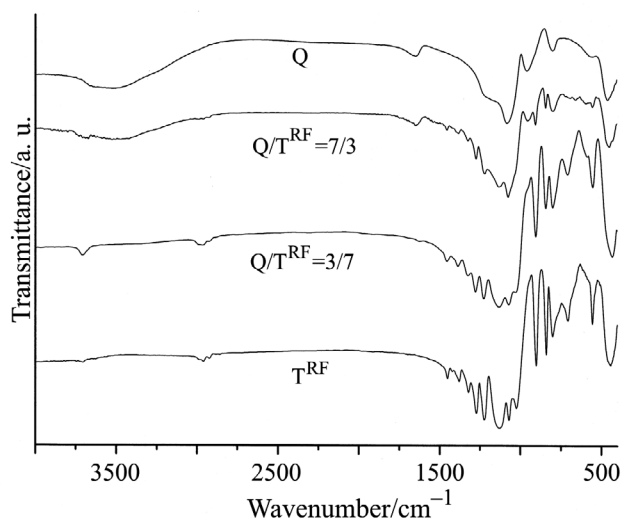


Fig. 1 FT-IR spectra of pure T^{RF} and Q gels in comparison with some mixed Q/T^{RF} gels chosen as representative examples

ported in Table 3. The F/Si experimental values are in agreement with the nominal composition of the specimens within the experimental error of the XPS technique (± 5 –10%). As concerns the behaviour under annealing, the different sets of fluorinated gels show a similar trend. In particular, the fluorine content shows a modest increase when the as-prepared gels are heated up to 400°C, and a more relevant decrease for the subsequent annealing up to 1000°C. The initial increase of the fluorine content could be attributed to the presence of not hydrolysed alkoxy and not condensed silanol groups inside the siloxane matrix, which are then released during heating in the first temperature range. A detailed analysis of the photoelectron lines suggests that a strong variation in the gel composition occurs during the second part of the thermal treatment (450–600°C), leaving a final fluorine content quite similar for all the 1000°C pyrolyzed samples, independently on their nominal Q/T^{RF} composition. The F1s line shows a similar peak position ($BE \approx 687.8$ eV) and a symmetric shape for all fluorinated gels heated at temperatures $\leq 400^\circ\text{C}$, whereas a significant broadening towards low BE values is only observed for samples annealed at higher temperatures. In the as-prepared samples the F1s signal is associated to the C–F bonds of the fluoroalkyl group of the silicon alkoxide precursor, as shown in Fig. 2. Such an attribution also agrees with the features of the C1s region, reported in Fig. 3, which reveals beside a major peak at 285.0 eV, associated to C–H alkyl units, a well defined minor component at 292.4 eV, typical of C–F bonds of fluorinated hydrocarbons [20]. After sample heating up to 1000°C the appearance of the low BE F1s component is accompanied by the disappearance of the high BE C1s component. These signal changes can be correlated to the fluorine migration from carbon to silicon sites with the formation of $\equiv\text{Si}-\text{F}$ bonds which yield SiO_xF_y units inside the

Table 3 Composition of as-prepared and annealed fluorinated gels as determined by XPS

Sample	Final temperature of thermal treatment/°C	Si/atomic%	F/atomic%	O/atomic%	C/atomic%	F/Si atomic ratio, experimental and (nominal ^a) value
Q/T ^{RF} =9/1	–	23.8	5.2	60.1	10.4	0.22 (0.30)
Q/T ^{RF} =9/1	400	20.5	7.2	52.9	18.5	0.35
Q/T ^{RF} =9/1	1000	23.5	4.1	58.2	13.7	0.17
Q/T ^{RF} =7/3	–	17.6	16.2	46.2	19.5	0.92 (0.90)
Q/T ^{RF} =7/3	400	19.0	18.6	42.8	19.4	0.98
Q/T ^{RF} =7/3	1000	22.8	3.7	54.4	19.0	0.16
Q/T ^{RF} =1/1	–	16.8	22.6	32.8	27.9	1.34 (1.50)
Q/T ^{RF} =1/1	400	15.9	26.5	33.5	24.1	1.67
Q/T ^{RF} =1/1	1000	22.7	4.7	54.2	18.3	0.21
Q/T ^{RF} =3/7	–	15.3	26.4	30.1	28.3	1.73 (2.10)
Q/T ^{RF} =3/7	1000	21.5	5.1	53.1	20.2	0.24
Q/T ^{RF} =1/9	–	12.1	33.0	20.7	34.1	2.73 (2.70)
T ^{RF}	–	11.5	38.2	18.5	31.6	3.32 (3.00)

^aValue calculated considering a fully condensed SiO₂ matrix

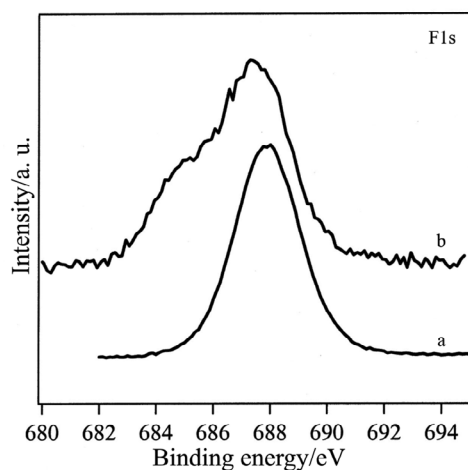


Fig. 2 XPS F1s region of $Q/T^{RF}=3/7$ gel: a – as-prepared sample and b – after heat treating up to 1000°C. Samples pyrolyzed at temperatures up to 400°C present the same F1s profile of curve a

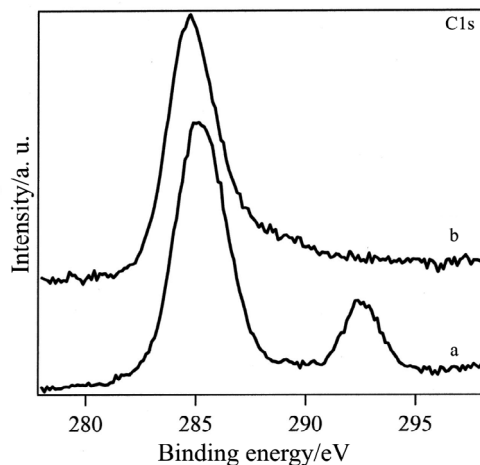


Fig. 3 XPS C1s region of $Q/T^{RF}=3/7$ gel: a – as-prepared sample and b – after heat treating up to 1000°C. Samples pyrolyzed at temperatures up to 400°C present the same C1s profile of curve a

siloxane structure whereas the minor F1s band centred at ca. 685 eV could be associated to fluorine atoms bonded to other vicinal siloxane chains through hydrogen bridging bonds [6]. Finally, the decrease of fluorine content in samples heated at the higher temperatures can be justified by the release of gaseous fluoroalkyl species (see thermal behaviour).

Pyrolysis of gels

TG-MS analysis data of the fluorinated silica gels are shown in Table 4. Table 5 reports all the chemical species identified in the TG-GC-MS analyses, carried out sampling 100 nm³ of evolved gas phase during the most representative mass losses. Among the detected compounds a large number of them has been identified by comparing their mass spectra with the ones of the pure substances recorded in the instrumental data base [21].

Thermogravimetric analysis of Q/T^{RF}=9/1 gel is characterized by a total mass loss of 24.3% in the 40–900°C range. The DTG curve shows two important thermal events; the first in the 40–400°C range centred at 100°C with a shoulder at 165°C, and the second in the 400–750°C range characterized by two partially overlapped bands centred at 540 and 590°C. The DTA curve presents a broad endothermic band corresponding to the first DTG peak at 100°C, followed by a sharp exothermic peak at 550°C. The TIC curve shows a trend, strictly correlated to the symmetric image of the DTG plot, with a broad asymmetric band centred at 185°C, a more pronounced sharp peak at 545°C, and a less intense one at 605°C, as reported in Fig. 4. The first thermogravimetric event (40–400°C) describes the typical behaviour of a SiO₂ gel synthesized starting from Si(OCH₂CH₃)₄, with evolution of EtOH, H₂O and traces of HCl. Actually, mass spectra recorded in this temperature range show the typical signal pattern of: EtOH *m/z* 46, 45, 31; H₂O *m/z* 18, 17; and HCl *m/z* 38, 37, 36, 35 (see insets *T*=125 and *T*=185°C of Fig. 4). All these species derive from condensation reactions between not hydrolysed groups (≡Si–OH; ≡Si–OCH₂CH₃; ≡Si–Cl) or, in less extent, from molecules physically entrapped inside the silica matrix [19]. The mass spectra corresponding to the second TIC peak at 545°C show the main evolution of CH₂=CH₂, with a minor amount of H₂O and fluorinated compounds such as CH₂=CHCF₃ and CH₂=CHCF₂H. All these compounds were initially identified by considering the signals corresponding to their molecular ions (i.e. *m/z* 28, 18, 96 and 78, respectively). These fluorinated hydrocarbons are also observed in the mass spectra corresponding to the last TIC peak at 605°C in which other signals at higher *m/z* values are detected.

A set of TG-GC-MS analyses were carried out in order to better identify all the evolved species. Gas chromatographic elutions of sampling at 100 and 185°C confirm the release of species observed in TG-MS analysis. On the other hand, elution at 540°C (Fig. 5) show the presence, along with H₂O and CH₂=CH₂, of several other compounds such as: fluorinated hydrocarbons CH₂=CHCF₃, CH₂=CHCHF₂, CH₃CH₂CF₃ (traces of CHF=CHF and HCF₃); oxygenated and/or dehydrogenated species CH₂=CHCHO (traces of CH₃CH₂CHO and CH₃COCH₃), which could derive from 'defluorination' reactions of the ≡Si–CH₂CH₂CF₃ group involving C–F/Si–O bond exchanges. Moreover, the observed evolution of CO₂, CO and CH₂=CHCH=CH₂ suggests the occurrence, at this temperature, of reactions with higher oxidation degree and cracking/reforming process of the evolved hydrocarbons. The same chemical species, with an increase of the amount of H₂O and CO, are observed in the sampling at 590°C, where the presence of a fluorinated silicon units such as F₂Si(CH₃)₂ is also detected.

Table 4 TG-MS analyses of $Q/T^{RF}=9/1$, $=7/3$, $=1/1$ and $=3/7$ samples. Thermogravimetric and DTA data. Species released in gas phase and identified^a by considering the mass spectra referring to the main TIC peaks

Sample	Total mass loss/%	Temperature of the 1 st TG event/°C; relative evolved species ^a	Temperature of the 2 nd TG event/°C; relative evolved species ^a	Temperature of further TG events/°C; relative evolved species ^a	Temperature of DTA events/°C
$Q/T^{RF}=9/1$	24.3	100 with shoulder at 165; EtOH, H ₂ O, HCl	540; CH ₂ =CH ₂ , H ₂ O, CH ₂ =CHCF ₃ , CH ₂ =CHCF ₂ H, EtOH, CH ₂ =CHCHO	590; H ₂ O, EtOH, CH ₃ CH ₂ CF ₃	100; endo 550; exo
$Q/T^{RF}=7/3$	36.4	140; EtOH, H ₂ O	535; CH ₂ =CH ₂ , H ₂ O, CH ₂ =CHCF ₃ , CH ₂ =CHCF ₂ H, CH ₃ CH ₂ CF ₃ , EtOH, CH ₂ =CHCHO	560 with shoulder at 610; CH ₂ =CH ₂ , H ₂ O, CH ₂ =CHCF ₃ , CH ₂ =CHCF ₂ H, CH ₃ CH ₂ CF ₃ , CH ₂ =CHCHO, F ₃ SiCH ₂ CH ₂ CF ₃	120; endo 515; exo 550; exo 580; exo
$Q/T^{RF}=1/1$	48.0	105; EtOH, H ₂ O	555; CH ₂ =CHCF ₃ , CH ₂ =CHCF ₂ H, CH ₃ CH ₂ CF ₃ , F ₃ SiCH ₂ CH ₂ CF ₃	—	580; exo
$Q/T^{RF}=3/7$	63.0	—	490 with shoulder at 430; CH ₂ =CHCF ₃ , CH ₂ =CHCF ₂ H, EtOH	570; CH ₂ =CHCF ₃ , CH ₂ =CHCF ₂ H, CH ₃ CH ₂ CF ₃ , F ₃ SiCH ₂ CH ₂ CF ₃	585; exo

^aThe identification of the released compounds were made on the basis of the detection of their molecular ions along with their fragmentation ions pattern

Table 5 TG-GC-MS analyses carried out sampling 100 nm³ of evolved gas phase during pyrolysis of the fluorinated silica gels

Sample	Sampling temperature/ ^o C, (relative mass loss/%)	Identified chemical species ^{a,b} (intensity/% ^c)
Q/Γ ^{RF} =9/1	100 (7.8)	H ₂ O (46), EtOH (54)
	164 (2.8)	H ₂ O (13), EtOH (87)
	540 (6.5)	CO (2), CO ₂ (1), HCF ₃ (t), C ₂ H ₄ (21), CHF=CHF (2), H ₂ O (21), C ₃ H ₆ (1), F ₂ CHCH=CH ₂ (5), F ₃ CCH=CH ₂ (8), F ₃ CCH ₂ CH ₃ (4), CH ₃ CHO (3), CH ₂ =CHCH=CH ₂ (1), EtOH (13), CH ₂ =CHCHO (16), CH ₃ CH ₂ CHO (2), CH ₃ COCH ₃ (t)
Q/Γ ^{RF} =7/3	590 (3.4)	[CO + CH ₄] (9), CO ₂ (3), C ₂ H ₄ (3), CHF=CHF (6), H ₂ O (41), C ₃ H ₆ (2), F ₂ CHCH=CH ₂ (2), F ₃ CCH=CH ₂ (1), F ₃ CCH ₂ CH ₃ (23), F ₂ Si(CH ₃) ₂ (4), EtOH (4), CH ₂ =CHCHO (2)
	140 (3.1)	H ₂ O (9), EtOH (91)
Q/Γ ^{RF} =7/3	535 (17.8)	[CO+CH ₄] (2), CO ₂ (1), HCF ₃ (1), C ₂ H ₄ (5), CHF=CHF (2), CF ₃ CH ₃ (2), H ₂ O (4), C ₃ H ₆ (1), F ₂ CHCH=CH ₂ (20), F ₃ CCH=CH ₂ (20), CH ₂ =CHCH ₂ F (t), CH ₂ =CFCH ₃ (t), F ₃ CCH ₂ CH ₃ (14), CH ₂ =CHCF ₂ CF ₂ H (5), F ₂ Si(CH ₃) ₂ (t), CH ₂ =CHCH=CH ₂ (t), CH ₂ =C(CH ₃)CF ₃ (t), CH ₂ =CFCH=CH ₂ (t), EtOH (13), CH ₂ =CHCHO (9), CH ₃ CH ₂ CHO (1), SiF ₄ (t), [isomers C ₅ ²⁻] (t)
	560 (10.5)	[CO+CH ₄] (1), CO ₂ (t), HCF ₃ (2), C ₂ H ₄ (6), CHF=CHF (3), CF ₃ CH ₃ (2), H ₂ O (5), C ₃ H ₆ (1), F ₂ CHCH=CH ₂ (20), F ₃ CCH=CH ₂ (25), CH ₂ =CHCH ₂ F (t), CH ₂ =CFCH ₃ (t), F ₃ CCH ₂ CH ₃ (14), CH ₂ =CHCF ₂ CF ₂ H (4), F ₂ Si(CH ₃) ₂ (t), CH ₂ =CHCH=CH ₂ (t), CH ₂ =C(CH ₃)CF ₃ (t), EtOH (4), CH ₂ =CHCHO (6), CH ₃ CH ₂ CHO (t), F ₃ SiCH ₂ CH ₂ CF ₃ (7), [isomers C ₅ ²⁻] (t)
Q/Γ ^{RF} =7/3	615 (1.5)	CH ₄ (3), CHF=CHF (3), H ₂ O (64), F ₂ CHCH=CH ₂ (2), F ₃ CCH=CH ₂ (2), F ₃ CCH ₂ CH ₃ (19), EtOH (7)

Table 5 Continued

Sample	Sampling temperature/ ^o C, (relative mass loss/%)	Identified chemical species ^{a,b} (intensity/%) ^c
Q/T ^{RF} =1/1	105 (1.8) 555 [46.2]	H ₂ O (100) [CO+CH ₄] (1), CO ₂ (t), HCF ₃ (1), C ₂ H ₄ (2), CHF=CHF (1), CF ₃ CH ₃ (2), H ₂ O (2), C ₃ H ₆ (1), F ₂ CHCH=CH ₂ (19), F ₃ CCH=CH ₂ (32), CH ₂ =CHCH ₂ F (t), CH ₂ =CFCH ₃ (t), F ₃ CCH ₂ CH ₃ (11), CH ₂ =CHCF ₂ CF ₂ H (4), F ₂ Si(CH ₃) ₂ - (t), CH ₂ =C(CH ₃)CF ₃ (t), CH ₂ =CFCH=CH ₂ (t), EtOH (t), CH ₂ =CHCHO (2), F ₃ SiCH ₂ CH ₂ CF ₃ (22), [isomers C ₅ ²⁻] (t)
Q/T ^{RF} =3/7	490 (29.3) 570 (33.7)	HCF ₃ (t), C ₂ H ₄ (t), H ₂ O (t), F ₂ CHCH=CH ₂ (63), F ₃ CCH=CH ₂ (22), MeOH (t), EtOH (15), [isomers C ₅ ²⁻] (t), C ₆ H ₅ CH ₃ (t) [CO+CH ₄] (t), CO ₂ (t), HCF ₃ (1), C ₂ H ₄ (1), CF ₂ =CF ₂ (t), CHF=CHF (1), CH ₂ =CHF (t), CF ₃ CH ₃ (2), H ₂ O (2), C ₃ H ₆ (1), F ₂ CHCH=CH ₂ (21), F ₃ CCH=CH ₂ (39), CH ₂ =CHCH ₂ F (t), CH ₂ =CFCH ₃ (t), F ₃ CCH ₂ CH ₃ (8), CH ₂ =CHCF ₂ CF ₂ H (2), CH ₂ =C(CH ₃)CF ₃ (t), CH ₂ =CFCH=CH ₂ (t), EtOH (t), CH ₂ =CHCHO (1), F ₃ SiCH ₂ CH ₂ CF ₃ (21), [isomers C ₅ ²⁻] (t), C ₆ H ₅ F (t)
Q/T ^{RF} =1/9	410 (13.2) 480 (73.6)	H ₂ O (29), MeOH (14), EtOH (57), C ₆ H ₅ -CF ₃ (t), C ₇ ²⁻ (t) H ₂ O (6), F ₂ CHCH=CH ₂ (74), F ₃ CCH=CH ₂ (20)

^aChemical species are listed in order of elution; their attributions were made on the basis of the comparison of the mass spectra with the ones of the pure substance available in the software data base of the mass spectrometer

^bChemical species eluted inside the same chromatographic peak are reported in square brackets

^cThe intensity of the eluted species, inside the same gas chromatogram, are approximately evaluated considering the area percentage values of their elutions peaks; t=traces

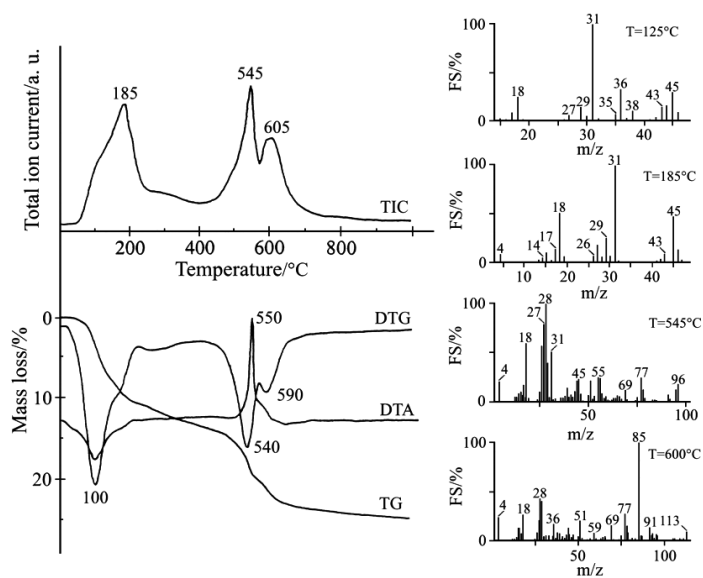


Fig. 4 Thermogravimetric mass spectrometric coupled analyses of Q/T^{RF}=9/1 gel. TG, DTG, DTA curves with the total ion current TIC plot of the evolved gas phase vs. pyrolysis temperature. In the insets mass spectra recorded at definite temperatures

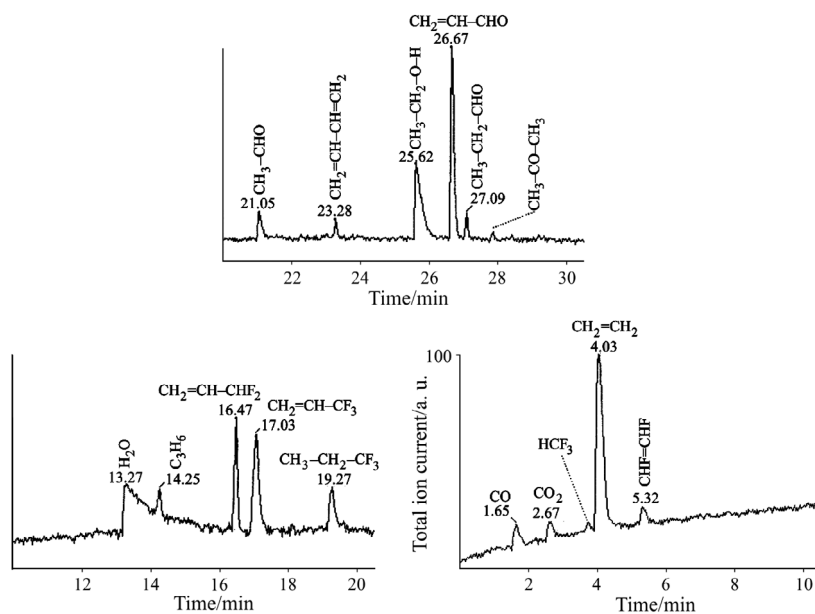


Fig. 5a Gas chromatographic elution of the gas phase released at 540°C during pyrolysis of Q/T^{RF}=9/1 gel (TG-GC-MS analysis)

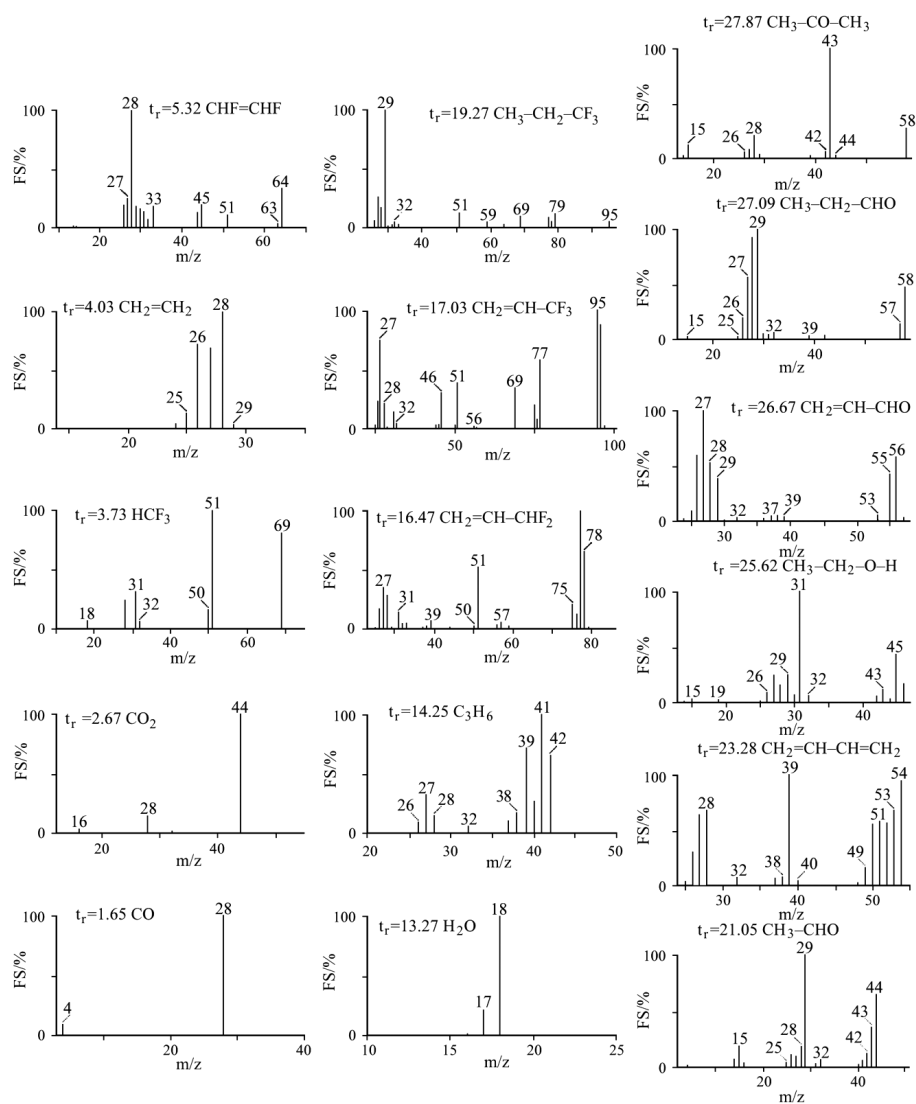


Fig. 5b In the insets mass spectra recorded corresponding to selected chromatographic peaks

The release of the main detected species during the whole pyrolysis process can be monitored through the trend of appropriate m/z ion currents, as shown in Fig. 6. EtOH is released in the 90–230°C range as evidenced by the very broad band of m/z 46 ion current of its molecular ion, and by the asymmetric band centred at 175°C of the most intense m/z 31 ion current due to the $[\text{H}_2\text{C}=\text{O}-\text{H}]^+$ fragmentation ion which is also

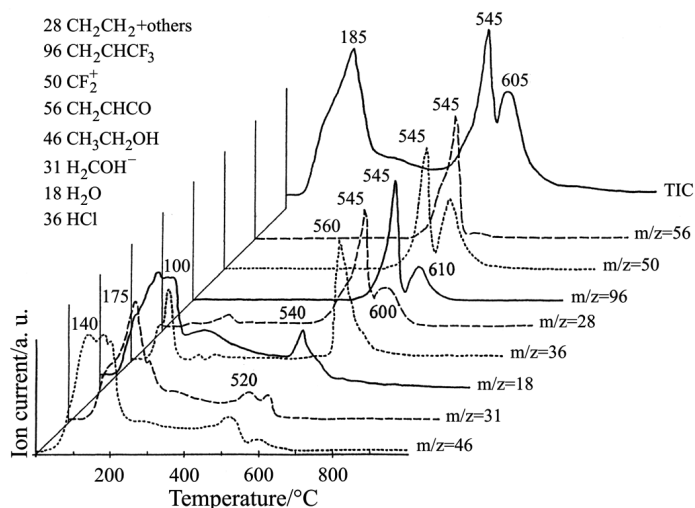
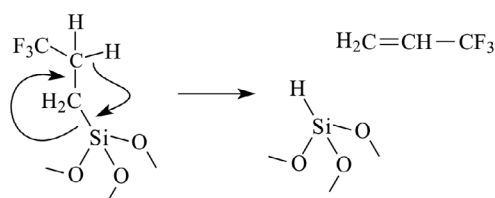


Fig. 6 Thermogravimetric mass spectrometric coupled analyses of $Q/T^{\text{RF}}=9/1$ gel. Ion currents of selected ions used to monitor specific evolved species during pyrolysis process

formed in the fragmentation process of CH_3OH molecule detected in traces. H_2O is released in the same temperature range (around 540°C) in a smaller extent; its evolution is monitored by its molecular ion ($m/z=18$). HCl release is detected both around 100 and 560°C , as shown by the ion currents of its isotopic pattern signals ($m/z=35, 36, 37, 38$). $m/z 28$ ion current shows a very sharp peak at 545°C followed by a less intense broad band at 600°C . This signal arises from both the $\text{CH}_2=\text{CH}_2$ release, usually observed around 540°C in silica gel samples, and the other species which are formed from the decomposition of the fluoropropyl group. Indeed, the simultaneous evolution of the main fluorinated hydrocarbons ($\text{CH}_2=\text{CHCF}_3$, $\text{CH}_2=\text{CHCHF}_2$) is revealed by the same trend of the ion currents of their molecular ions ($m/z 96$ and 78 , respectively); these signals show two subsequent bands centred at 545 and 610°C . Moreover, the same trend is also observed for the ion currents of $m/z 69, 51$ and 50 signals, attributed to the CF_3^+ , CHF_2^+ and CF_2^+ fragmentation ions, respectively. This fact indicates that all the fluorinated compounds are released inside these two thermal events, because these fragmentation ions could be formed from any of the detected fluorinated species. On the other hand, the oxygenated species arising from the decomposition of the fluoropropyl group ($\text{CH}_2=\text{CHCHO}$ and $\text{CH}_3\text{CH}_2\text{CHO}$) are detected only during the former of these thermal events, as shown by the sharp band centred at 540°C of both of the ion currents of their molecular ions ($m/z 56$ and 58 signals, respectively).

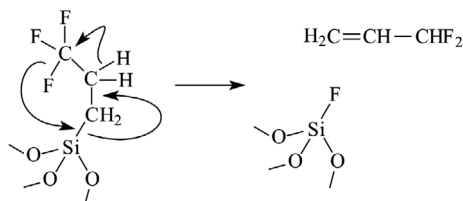
The thermal behaviour of the other Q/T^{RF} samples is strictly correlated with the one of the previously reported pyrolysis, so that the experimental data will be presented and discussed together for all the gels. Thermogravimetric analysis of $Q/T^{\text{RF}}=7/3, =1/1$, and $=3/7$ samples presents a regular trend, with an exponential de-

crease of the intensity of the first event and a linear increase in the second one with the increase of the of T^{RF} precursor amount in the gel matrices, as shown in Fig. 7. In these samples, characterized by a higher fluorine content, the release of silicon units with Si-F bonds, such as $F_3SiCH_2CH_2CF_3$ and SiF_4 , are also observed. The evolution of the fluorinated species, described for the various gel samples by means of their relative TIC curves shown in Fig. 8, deserves some comments. Although in absence of specific mechanistic studies but on the basis of the thermal behaviour observed in the case of gels characterized by differently functionalized alkyl groups, some reactions are proposed in order to explain the main released species. $CH_2=CHCF_3$ could derive by an elimination reaction from the $SiCH_2CH_2CF_3$ group by means of a 1, 3 hydrogen transfer from the central carbon to the silicon atom:



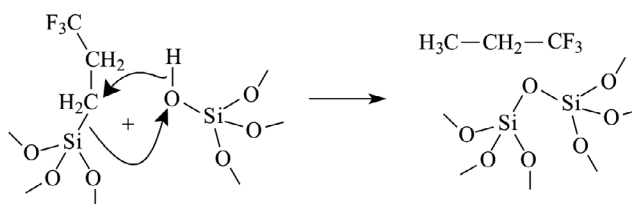
Equation (1)

Similarly, $CH_2=CHCHF_2$ could be formed by considering a 1,4 fluorine migration to the silicon atom, according to its intrinsic strong coordination, along with a 1,2 hydrogen transfer to the terminal carbon atom:



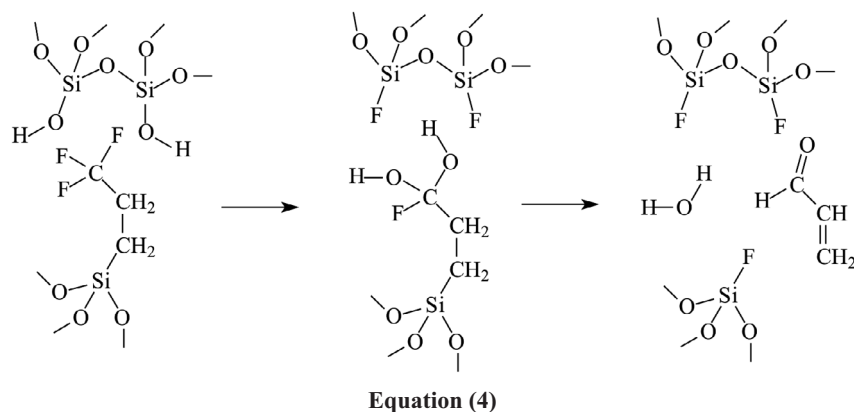
Equation (2)

On the other hand, taking into account the interaction among the siloxane chains inside the gel structure, $CH_3CH_2CF_3$ release could derive from condensation reaction between vicinal $\equiv Si-OH$ and $\equiv Si-CH_2CH_2CF_3$ groups:



Equation (3)

Actually, the presence of such saturated and fluorinated hydrocarbon is higher in the gels prepared with a relevant amount of tetraethoxysilane, leading to gel matrices richer in residual hydroxyl groups as shown by IR data. In fact, in absence of a significant amount of $\equiv\text{Si}-\text{OH}$ groups, such as in the case of $Q/T^{\text{RF}}=1/9$ and $Q/T^{\text{RF}}=3/7$ samples, the release of this fluorinated hydrocarbon is not detected (confirming the hypothesis that its occurrence requires both groups) and only the products arising from an intramolecular silicon-unit elimination can be formed (i.e. Eqs (1) and (2)). This fact is even more evident in the formation of oxidized species, where the reiterated 'defluorination' reactions requires the presence of a higher number of silanol groups. Indeed, the release of $\text{CH}_2=\text{CHCHO}$ could be described, for example, by subsequent reactions involving: (i) C-F/Si-OH bond exchange between vicinal fluoroalkyl and silanol groups; (ii) water elimination from geminal hydroxyl groups; (iii) elimination of the alkyl group as previously described in Eq. (2).



Moreover, the occurrence of reiterated Si-O/C-F bond exchange reactions inside the siloxane network is also demonstrated by the release of silicon fluorinated species such as $\text{F}_3\text{SiCH}_2\text{CH}_2\text{CF}_3$ and SiF_4 . These compounds are detected in more extent in the pyrolysis of $Q/T^{\text{RF}}=7/3$ and $=1/1$ samples. Indeed, these specimens show experimental mass losses greater than the theoretical values which can be calculated by considering only the complete elimination of the fluorine-alkyl group from fully condensed silica matrices (Fig. 7). The release of these fluorinated silicon units also justify the drastic decrease of the fluorine content remaining in the solid matrices after the pyrolysis process, as revealed by XPS data. On the other hand, the release of these silicon units involves relevant rearrangements into the silica skeleton leaving new cavities, which are responsible for the slight increase of the specific surface area values observed in the samples heated at temperatures higher than 600°C (Table 2).

A different thermal behaviour is observed for $Q/T^{\text{RF}}=1/9$ and $T^{\text{RF}}(\text{NH}_3)$ samples. In the first case, the pyrolysis process yields a total mass loss of 86.8%. TG and DTG curves show a main event inside the $250\text{--}650^\circ\text{C}$ range, centred at 480°C with a shoulder at 410°C , preceded by three small bands in the $50\text{--}380^\circ\text{C}$ range. The TIC

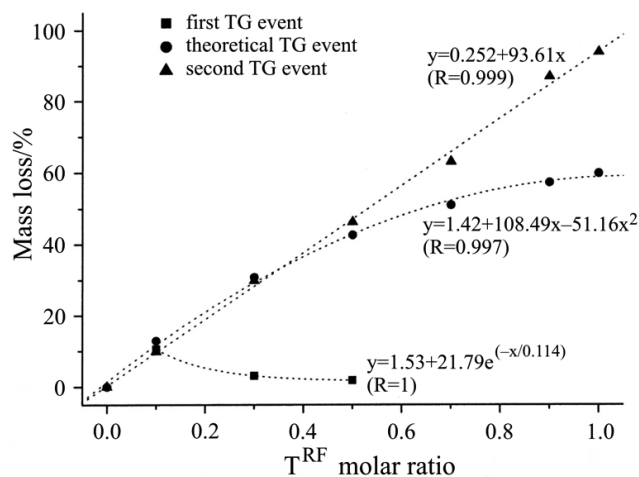


Fig. 7 Thermogravimetric analyses in the pyrolysis of the Q/T^{RF} gels. Mass losses values recorded during the first event (condensation reactions), the second event (elimination reactions) in comparison with the theoretical values calculated for a total fluorine alkyl elimination from fully condensed silica matrices

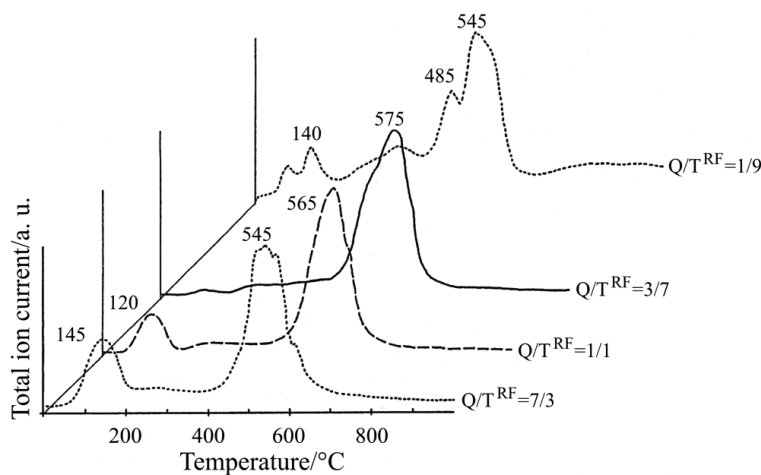


Fig. 8 Thermogravimetric mass spectrometric coupled analyses of Q/T^{RF} gels. Total ion current TIC plots of the evolved gas phase vs. pyrolysis temperature

curve presents the same trend, showing three small peaks centred at 80, 140 and 360°C related to the evolution of H_2O , CH_3OH and CH_3CH_2OH , respectively, whereas, the release of fluorinated species ($CH_2=CHCHF_2$ and $CH_2=CHCF_3$) is observed during the more intense TIC band at 545°C.

The thermogravimetric analysis of T^{RF} gel only shows a drastic mass loss (93.7%) centred at 395°C (220–430°C range). On the other hand, the TIC curve is characterized

by a completely different trend, only showing two very small peaks at 100 and 180°C corresponding to the evolution of H₂O and CH₃OH. This atypical behaviour indicates that T^{RF} sample, during pyrolysis process, does not undergo the usual siloxane chain rearrangements involving condensation and elimination of non-hydrolysed groups. These facts suggests that the T^{RF} sample could be formed by a network containing, besides oxygen bridging bonds, interactions such as ≡Si-CH₂CH₂CF₂-F···HOSi≡ which could confer to the sample the features to sublimate. As a matter of fact, in the pyrolysis of the T^{RF} sample stopped at ca. 400°C, the FT-IR spectra recorded on solid fractions of specimens recovered both inside the crucible-sample and deposited on the sample-thermobalance-road, show an absorption pattern almost identical to the untreated T^{RF} gel sample.

Conclusions

Silica based gels with different fluorine content were prepared by hydrolysing mixtures of CF₃CH₂CH₂Si(OCH₃)₃ and Si(OCH₂CH₃)₄ of different molar ratios. Samples, obtained as transparent monolithic objects, were physically and chemically stable in air at room temperature. The gelling process, carried out in a strong acidic medium, yielded silica matrices with a total retention of the fluoroalkyl groups. On the other hand, an incomplete hydrolysis and condensation was observed for the alkoxy groups, and in particular for the ethoxyl moieties of the Si(OCH₂CH₃)₄ precursor.

TG-MS and TG-GC-MS analyses allowed a qualitative description of the chemical composition of the crude gel matrices and the main chemical rearrangements occurring in the solids during the pyrolysis process. The observed pyrolysis behaviours well agreed with the morphological features of both crude and annealed gel samples. Residual alkoxy groups, present in more extent in gels with higher Q/T^{RF} molar ratio values, were first easily released from the solid matrices by reaction with not condensed silanol groups in the 100–250°C range. Water was also released by condensation reactions leading to a drastic decrease of the ≡Si-OH groups. Ethoxyl groups still surviving this process were subsequent decomposed by elimination of ethene around 540°C.

The release of the fluoroalkyl groups was observed at temperatures higher than 450°C following various pathways, and yielding several different compounds depending on the Q/T^{RF} molar ratio of the initial gels. The main released species were unsaturated fluoropropyl compounds in which the original fluorine content was almost totally conserved. Gel prepared with a higher percentage of Q precursor showed the evolution of relevant amounts of oxygenated olefins. The formation of these latter species previously required a total loss of the fluorine atoms by C-F/Si-O bond exchanges. For the intermediate Q/T^{RF} gel compositions, the same C-F/Si-O bond exchange reactions led to the release of fluorinated silicon units also still retaining the original fluoroalkyl group.

The loss of silicon units along with the high number of different and variously fluorinated species (with similar mass spectra) did not allow to process the experimental TG-MS data in order to quantify the amounts of released species and to deduce a chemical formula for the description of the composition of the initial gel network.

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