FTIR THERMAL ANALYSIS ON ANILINEPROPYLSILICA XEROGEL

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Abstract

FTIR thermal analysis was used for a hybrid xerogel, anilinepropylsilica, obtained from three different organic precursor amounts, using HF and NaF as catalysts in the sol–gel process. The aniline ring vibrational mode at 1500 cm^{-1} of attached aniline groups was used to obtain the relative aniline content in the xerogel materials after being submitted to thermal treatment in the temperature range from 100 to 400°C. This technique allowed to evaluate the thermal stability of organic phase. The organic coverage on the surface and the fraction of trapped organic groups in closed pores can also be evaluated.

Introduction

Organofunctionalized silica materials received special attention in the last years due to the great potential applications specially in separation science as adsorbents for SPE (solid phase extraction) or stationary phase for chromatography [1–5]. The sol–gel method [6] has been an important route to prepare these materials using alkoxysilanes R-Si(OR)$_3$ and tetraethylorthosilicate (TEOS) or tetramethylorthosilicate (TMOS) as precursors. The polycondensation of alkoxysilanes can be described in three reactions: i) hydrolysis; ii) silanol–silanol and silanol–alcohol condensation [7–10]. The simplicity and versatility of the sol–gel process for obtaining organofunctionalized silica materials, associated with the possibility of controlling the morphological properties, like surface area, particle shape and size, and organic functionalization grade, are some of the advantages of this process [8, 11]. In the polycondensation reaction, fluoride ion is very often used as nucleophilic catalyst [10, 12, 13] and it can be utilized in different forms like HF, NH$_4$F, NaF, etc. When sodium fluoride is used, changes in the morphological properties of the gel have been observed [14–16] and they are not completely understood.

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The thermal analysis is a useful tool to study the interaction strength between the attached groups and the surface of matrix [1, 17–23]. Among the thermal analyses TG (thermal gravimetric analysis) is widely used in these systems because this technique allows also an evaluation of the organic content attached to the surface. However, by using TG it is difficult to differentiate between the organic desorbed groups and water mass loss produced by the dehydroxylation reaction of the surface, which takes place with the increasing temperature [24–26]. Additionally, the fraction of organic groups trapped in closed pores cannot be evaluated. For materials containing organic groups that present characteristic infrared absorption bands these difficulties can be overcome. It was already demonstrated in a recent paper [11] that infrared analysis can be used to estimate the comparative organic content in organo-functionalized silica materials because the infrared band areas of the immobilized groups are related to the organic content. In this work, we have used FTIR thermal analysis that allows the investigation of the organic groups attached to the surface, using their specific infrared band. It is possible to evaluate the thermal stability and also the fraction of trapped organic groups in the closed pores of the materials. In this work it was studied the anilinepropylsilica xerogel that was synthesized using two different catalyst precursors, HF and NaF.

Experimental

Synthesis anilinepropylsilica xerogels [27]

Aniline was activated with sodium hydride in 10 mL of the aprotic solvent mixture (toluene:thf) (1:1) for 30 min and then the chloropropyltrimethoxysilane (CPTMS) was added. The quantities used were stoichiometric for CPTMS, aniline and NaH. The product of reaction, anilinepropyltrimethoxysilane (APTMS) was used as organic precursor of the xerogel in the concentration of 1.2, 4.0 and 9.0 mmol L^{-1} for the synthesis 1, 2 and 3, respectively. The mixture was stirred under argon at solvent-reflux temperature during a period of 5 h. After that, 5 mL of tetraethylorthosilicate (TEOS), 5 mL of ethyl alcohol, 1.6 mL of water (stoichiometric ratio $H_2O/Si=4$) and HF or NaF (4 mmol), were added to the precursor solutions, under stirring. The pH values of the mixtures were basic ca 9. The mixture was stored during 5 days at room temperature just covered without sealing, for gelation and evaporation of solvent. The gel was then washed with toluene, thf, methyl alcohol, water and ethyl ether. The resulting material was dried for 30 min in an oven at 100°C and comminuted in an agate mortar for subsequent infrared analysis.

Infrared thermal analysis

Self-supporting disks of the material to be analyzed were prepared, with an area of 5 cm^2, weighting ca 100 mg. The disks were heated in a temperature range from 100 to 400°C under vacuum (10^{-3} Torr), from 1 to 6 h. The IR cell used in this work present two sections, an oven that consists of an electrical filament on the external wall of

the cell and another section with two KBr windows for submitting the sample to the infrared beam, using a mobile support. The two sections are pressed together using a viton O-ring. The sample can be heated up to 400°C, under vacuum and then moved to the infrared beam. Thus the sample is not exposed to the external environmental [28]. The equipment used was a Shimadzu FTIR, model 8300. The spectra were obtained with a resolution of 4 cm^{-1}, with 100 scans. The materials obtained by using HF and NaF as catalyst precursors were designated XHFn and XNaFn, respectively, where *n* specify the synthesis.

Results

The vibrational mode of aniline ring at 1500 cm^{-1} is very strong in the spectra, so the band area of this absorption was used to estimate the thermal stability of the immobilized aniline groups on the silica surface. The silica overtone band at ca 1865 cm^{-1} was used as a reference band [11]. This normalization was necessary, considering the heterogeneity in the disks thickness and taking into account the position changes of the infrared beam.
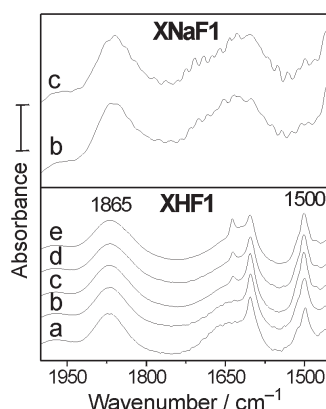

Fig. 1 Infrared spectra of xerogel samples obtained by synthesis 1, after heating in vacuum, for 6 h at: a – 100; b –200; c – 300; d – 350 and d – 400°C. The bar value is 0.2 and 0.1 for the spectra of the xerogels XHF1 and XNaF1, respectively

FTIR spectra of xerogels obtained at room temperature, previously heat treated for 6 h, in the temperature range from 100 to 400°C, are shown in Figs 1, 2 and 3 for the synthesis 1, 2 and 3, respectively. In XNaF1 sample, prepared with low amount of organic precursor (synthesis 1) and NaF as a catalyst, the organic groups were not incorporated in the gel (Fig. 1). For the XHF1 sample, prepared without NaF, the organic phase was incorporated, because the aniline band modes are present in the spectra even after thermal treatment (Fig. 1 and Table 1). Since the organic band areas are related to the organic content, for the synthesis 2 and 3, where a greater precursor amount was added, an increase in the organic content was observed (Figs 2, 3 and Table 1). However, for the sample XNaF2, which NaF was used as a catalyst, a lower

organic content was observed when compared with the sample XHF2 catalyzed with HF (Table 1). In the XNaF3 and XHF3samples the decrease in the organic incorporation, produced by Na$^+$ presence, is not observed (Table 1).
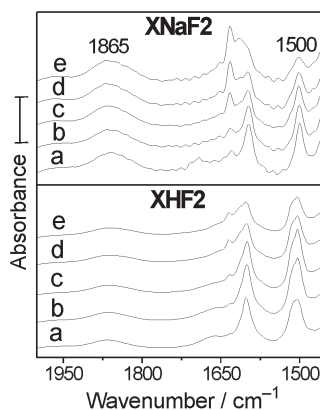

Fig. 2 Infrared spectra of xerogel samples obtained by synthesis 2, after heating in vacuum, for 6 h at: a – 100; b –200; c – 300; d – 350 and d – 400°C. The bar value is 1 and 0.4 for the spectra of the xerogels XHF2 and XNaF2, respectively
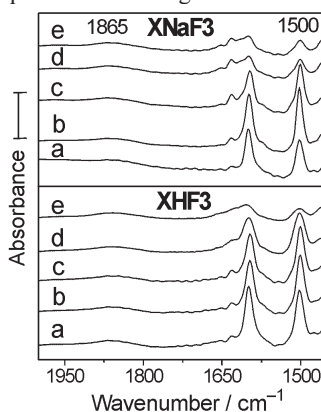

Fig. 3 Infrared spectra of xerogel samples obtained by synthesis 3, after heating in vacuum, for 6 h at: a – 100; b –200; c – 300; d – 350 and d – 400°C. The bar value is 1 for the spectra of the xerogels XHF3 and XNaF3

The relative remaining organic grades obtained using the band area values (Table 1), are presented in Fig. 4. Six values were obtained for each temperature of treatment (1–6 h) for each sample. All the samples maintain 100% of the organic content after heat treatment up to 200°C for 6 h. The organic grade begins to decrease for samples obtained from synthesis 2 and 3 after thermal treatment at 300°C (Table 1). This decrease was more visible for XNaF2 and XNaF3 (Figs 2 and 3). All the samples present a remaining organic grade even after heat treatment up to 400°C for 6 h. This remaining organic grade was inversely related to the organic content (Fig. 4).

Table 1 Infrared band areas of aniline ring mode at 1500 cm^{-1} on xerogel materials and the relative remaining organic grade calculated from these band areas

Temp./ °C	Time/ h	Band area[1] (Relative remaining organic grade/%)				
		XHF1	XHF2	XNaF2	XHF3	XNaF3
100	6	0.34	2.02	0.54	2.54	2.32
200	1	0.40(100)	2.06(100)	0.60(100)	2.61(100)	2.65(100)
	2	0.39(98)	2.06(100)	0.59(98)	2.61(100)	2.63(99)
	3	0.39(98)	2.07(100)	0.60(100)	2.61(100)	2.63(99)
	4	0.40(100)	2.06(100)	0.58(97)	2.63(101)	2.61(98)
	5	0.39(98)	2.04(99)	0.57(95)	2.63(101)	2.61(98)
	6	0.40(100)	2.06(100)	0.57(95)	2.51(96)	2.55(96)
300	1	0.42(105)	2.03(99)	0.53(88)	2.50(96)	2.48(94)
	2	0.40(100)	2.04(99)	0.52(87)	2.51(96)	2.23(84)
	3	0.42(105)	2.03(99)	0.48(80)	2.51(96)	2.32(88)
	4	0.41(103)	2.02(98)	0.48(80)	2.52(97)	2.14(81)
	5	0.42(105)	2.00(97)	0.48(80)	2.49(95)	2.11(80)
	6	0.41(103)	1.98(96)	0.46(77)	2.46(94)	2.09(79)
350	1	0.41(103)	1.86(90)	0.46(77)	2.43(93)	1.47(55)
	2	0.38(95)	1.77(86)	0.40(67)	2.41(92)	1.43(54)
	3	0.38(95)	1.67(81)	0.42(70)	2.38(91)	1.16(44)
	4	0.40(100)	1.44(70)	0.40(67)	2.31(89)	1.01(38)
	5	0.40(100)	1.43(69)	0.38(63)	2.17(83)	0.95(36)
	6	0.39(98)	1.41(68)	0.40(67)	2.17(83)	0.89(34)
400	1	0.37(93)	1.30(63)	0.25(41)	1.80(69)	0.91(34)
	2	0.36(93)	1.31(64)	0.26(43)	0.73(28)	0.85(32)
	3	0.35(88)	1.20(58)	0.24(40)	0.63(24)	0.79(30)
	4	0.35(88)	1.20(58)	0.24(40)	0.64(25)	0.73(28)
	5	0.34(85)	1.03(50)	0.25(41)	0.63(24)	0.71(27)
	6	0.34(85)	1.04(50)	0.25(41)	0.63(24)	0.71(27)

[1] – band areas of aniline mode at 1500 cm^{-1}, normalized with the silica overton band at 1865 cm^{-1}

Discussion

Considering that the organic band areas are related to the organic content of the xerogel materials, we observed that the organic content was related to the amount of the organic precursor added, since the band areas increase from synthesis 1 to 3 (Table 1). It was also observed that the Na$^+$ presence reduces the organic content for the samples from synthesis 1 and 2, with a low amount of organic precursor added (Figs 1, 2 and Table 1).

The relative remaining organic grade indicates the thermal stability of the organic attached groups. The great organic thermal stability observed for the samples heat treated up to 300°C is an evidence that these groups are strongly bound to the surface in the covalent form. Further thermal treatment up to 400°C produces a partial organic desorption from the surface, as observed by the area reduction (Table 1 and Fig. 4). It was possible to observe that the samples catalysed with NaF present lower thermal stability than the samples synthesized without sodium. It is more evi-

dent for synthesis 3 where the organic grade decrease begins at 300°C for XNaF3 sample while for XHF3 this decrease occurs after heating up to 400°C (Fig. 4). Therefore, the more stable organic phase was obtained by using HF as a catalyst and high organic precursor concentration i.e. for XHF3 sample. This fact can be explained taking into account that the more concentrated the APTMS precursor is, the closer the reactive organic methoxysilane groups will be and the easier the linkage process occurs [11]. Therefore, for larger concentration of APTMS added, the organic phase is more thermally stable, since a more linked organic structure was formed in the gelation process. Na$^+$ influence was interpreted as an inhibitor of the organosilane linkage by avoiding its proximity [29]. This interpretation may explain also the absence of the infrared organic band in the XNaF1 sample, obtained from synthesis 1, with lower organic precursor concentration and catalysed by NaF.

All the samples present a residual fraction of organic groups even after thermal treatment for six h at 400°C (Table 1 and Figs 1–4). This fact can only be explained by taking into account the retention of the organic phase in closed silica pores formed during the polycondensation and drying process. Considering the band area values found for the sample XHF1, after heat treatment at 400°C, we can deduce that 85% of the organic groups are trapped in closed pores (Fig. 4). The samples obtained from synthesis 2 present a lower fraction of organic trapped groups, 50 and 41% for XHF2 and XNaF2, respectively. For the samples with higher organic loading the trapped organic groups fraction was the lowest, 24 and 27% for XHF3 and XNaF3, respectively (Fig. 4 and Table 1). Therefore, the increase in the organic content results in a decrease in the fraction of organic trapped groups.
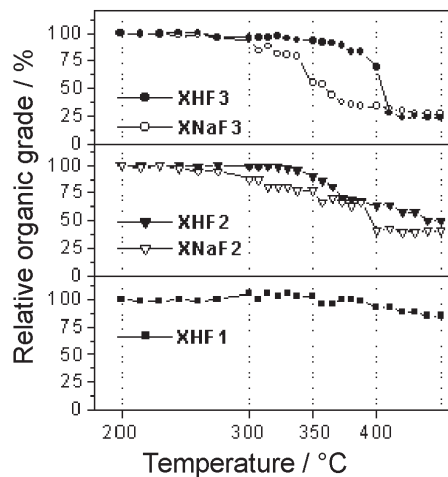

Fig. 4 Relative remaining organic grade calculated from the relative band area of the infrared aniline band at 1500 cm^{-1} in relation to the thermal treatment of the xerogels obtained from synthesis 1–3 using HF and NaF as precursor catalysts. For each temperature of treatment six measurements were made (1–6 h)
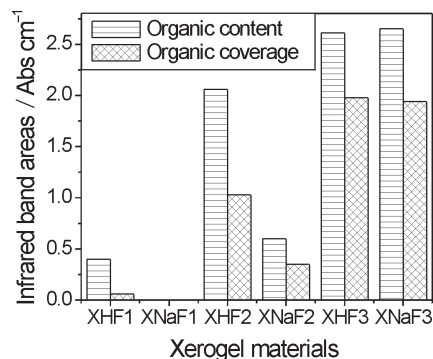
Fig. 5 Relative organic content and organic coverage of the xerogel materials calcu-
lated from the band areas of the infrared aniline mode at 1500 cm^{-1}

From the band areas of FTIR spectra it was possible to calculate the relative or-
ganic coverage i.e. organic groups that are really on the surface, in opened pores. It
was obtained subtracting the band area corresponding to the organic trapped groups
from band areas of the organic total content. The resulting organic coverage is pre-
sented in Fig. 5. As the organic loading increases with the organic precursor concen-
tration added (from synthesis 1 to 3) and simultaneously a decrease occurs in the oc-
cluded porous fraction, the samples that present higher organic coverage are those
obtained from synthesis 3. The crescent organic coverage with the organic loading
(Fig. 5) was interpreted considering that the increase in the APTMS/TEOS precursor
ratio produces a less cross-linked silica network that results in a larger fraction of
opened pores [30–32].

Conclusions

FTIR thermal analysis technique was very effective to find better synthesis condi-
tions for anilinepropylsilica xerogel material, regarding to achieve a higher organic
content, organic coverage and thermal stability. These characteristics, which are im-
portant for materials with potential applications in separation sciences, were obtained
using high organic precursor amount and HF as a catalyst.

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