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Studies of the hydrolysis of ethyl and *tert*-butyl phosphonates covalently bonded to silica xerogels

Céline Carbonneau, Richard Frantz, Jean-Olivier Durand,* Michel Granier, Gérard F. Lanneau* and Robert J. P. Corriu

Laboratoire de Chimie Moléculaire et Organisation du Solide, UMR 5637, case 007, Université Montpellier 2, Place Eugène Bataillon, 34095 Montpellier cedex 05, France. Fax: 04-67-14-38-52; E-mail: durand@univ-montp2.fr; E-mail: lanneaug@univ-montp2.fr

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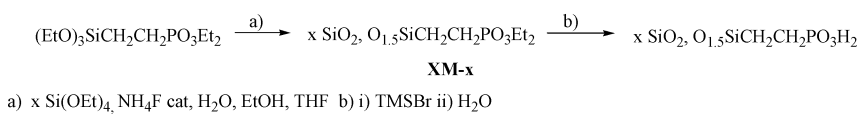
The mild cleavage of phosphonodiester groups supported on a silica matrix has been investigated. The use of TMSBr (bromotrimethylsilane) with diethyl phosphonates has been revisited, and interactions of phosphonoacids with silicon species are described. An alternative route utilising di-*tert*-butyl phosphonate group has also been studied and in this case cleavage has been demonstrated in very mild conditions.

Introduction

The syntheses and design of silica-based materials by using sol–gel chemistry have grown a lot in the last few decades.[1] Silica materials possessing a covalently bonded carboxylic acid group have recently received attention for their potential use as silica stabilizers,[2a] metal complexants[2b] and supported catalysts.[2c,d] In this context, silica based phosphonic acid groups would be of high interest and would find use in ion detection and chromatographic devices.[3] Furthermore, phosphonates and phosphonic acids proved useful building blocks for the elaboration of hybrid organic–inorganic materials,[4a–c] for the generation of self-assembly mono and multilayers,[4d–g] and for grafting on metal oxides.[4h–j] Thus, silica based phosphonic acids would be valuable for preparation of materials possessing a SiO_2 matrix covalently bonded to another oxide (Al_2O_3, SnO_2, TiO_2). However, very few studies of the hydrolysis of diethyl phosphonate esters covalently bonded to silica surfaces have been reported in the literature. Page and co-workers[5] have described 10-(diethoxyphosphoryl)decylphosphonic acid self-assembled onto Hf functionalised Cab-O-Sil to give high surface silica with surface phosphonate ester groups. The diethyl phosphonate ester surface groups were efficiently hydrolyzed by refluxing in 3 M HCl for 7 or 2 h, whereas TMSBr–LiI in MeCN for 7 h seemed to be inefficient, based on MAS ^{31}P solid state NMR analysis. Blanchard[6] has hydrolysed isopropyl phosphoesters on polymer multilayers grafted on silica by their phosphate groups. TMSBr in MeCN at RT proved efficient based on ^{31}P MAS solid-state NMR analysis. Comparing with the results of Page,[5] Blanchard[6] explained that the availability of phosphoesters in his polymers was probably higher. Chevalier and coworkers[7] have hydrolyzed ethyl phosphonate covalently grafted on the silica surface of ion sensitive field-effect transistor grids by depositing on the grid one drop of TMSBr at 60 °C, for 3 h. The silylated phosphonic acid intermediates were then hydrolyzed by water at room temperature. Spectroscopic analyses concerning the cleavage were not reported. Sullivan and co-workers[8] have synthesized hybrid organic–inorganic materials with covalently bonded phosphonates, by using the acid-catalysed sol–gel procedure. Hydrolysis of the phosphonate moiety was performed by refluxing in 12 M HCl for 24 h. The cleavage was proved by ^{13}C and ^{31}P MAS NMR. Interactions between phosphonate/phosphonic acid groups and silica were briefly mentioned. In view of the literature, the cleavage of supported diethyl phosphonate ester groups on silica seems to be best performed by using harsh conditions (refluxing 3 or 12 M HCl). We present here our studies to find mild and general conditions for hydrolysis of silica-supported dialkyl phosphonates, compatible with sensitive, functionalized organic backbones such as arylene–vinylene chromophores.[9] Interactions of phosphonic acids with silica were investigated, based on solid-state MAS NMR analyses and previous reports[10] concerning bonding of free phosphonic acids onto surfaces of metal oxides[10a,b,4j] and silica.[10c,d] Hydrolysis of supported di-*tert*-butyl phosphonate esters, which are easily cleaved in the homogeneous liquid state, has not been reported on supported materials based on silica, and is described as well.

Results and discussion

The cleavage of diethyl phosphonate esters in solution is well documented.[11] The usual treatment involves the reflux of 6 M HCl.[11a] Alternatively, treatment by TMSI[11b,c] (iodotrimethylsilane) or TMSBr[11c,d] in MeCN or CH_2Cl_2 at RT followed by hydrolysis or methanolysis proved a milder and more selective way to cleanly obtain phosphonic acid derivatives. However these reactions are not necessarily efficient when one of the reactants is confined to a surface, as shown by Page.[5] We thus decided to revisit the use of TMSBr, to find the conditions where this reagent works. We first studied the conditions of the cleavage on the model co-gels $x SiO_2$, $O_{1.5}Si(CH_2)_2PO_3Et_2$ **XM-x** (Scheme 1). Hovnanian[12] and Sullivan[8a] have described the HF-catalyzed and the HCl-catalyzed gelation of phosphonoethyltriethoxysilane respectively. We have used the nucleophilic-catalyzed (NH_4F) co-gelation procedure[9b] of (diethoxyphosphorylethyl)triethoxysilane (Scheme 1).



Scheme 1 Gelification of (diethoxyphosphorylethyl)triethoxysilane, hydrolysis of the phosphonate function.

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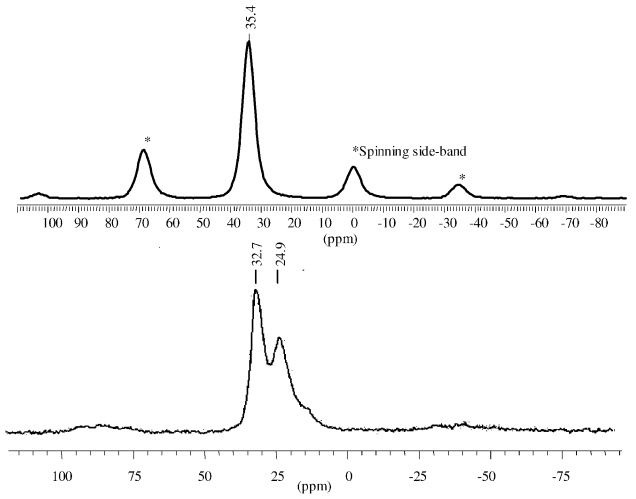


Fig. 1 HPDEC MAS ^{31}P NMR (161 MHz) of **XM-17.5** and of **XM-17.5** after treatment by TMSBr and H_2O.

The precursor was dissolved in a mixture of EtOH and THF (50 : 50) in the presence of various amounts of TEOS ($x = 1$ to 20). The concentration of the silicon derivatives was between 0.5 and 1 M. After addition of $(1.5 + 2x)$ moles of water and a catalytic amount of NH_4F 0.25 M in water, transparent gels were formed within a few days at RT. After curing for 5–7 days at RT, the gels **XM** were powdered, washed with THF, EtOH, Et_2O, and dried at 120 °C overnight under vacuum. Gels were well condensed as seen from CP MAS ^{29}Si NMR studies (major signals: T_3, Q_3, Q_4, see experimental). Cleavage of the phosphonate ester was performed on co-gels **XM-2**, **XM-5**, **XM-10**, **XM-17.5** by using pure TMSBr. Different temperatures were tested from 120 to 50 °C; the reaction worked in every case, and lower temperatures were not studied. Reaction with co-gel **XM-17.5** is representative. **XM-17.5** was treated by TMSBr at 50 °C for 24 h in a sealed tube. After evaporation of TMSBr, the material was particularly hydrophobic and was stirred in water for 3 days at RT, then dried under vacuum at 120 °C overnight. Solid-state HPDEC MAS (high power decoupling magic angle spinning) ^{31}P NMR of phosphonate **XM-17.5** and of phosphonate **XM-17.5** after treatment by TMSBr and water at RT (**XM-17.5Si**) are presented in Fig. 1. The starting material **XM-17.5** presented only one symmetric signal at 35.4 ppm indicating a homogeneous environment of the phosphonate ester. The treatment modified the spectrum and **XM-17.5Si** presented two significant signals at 32.7 and 24.9 ppm which were respectively attributed to the free phosphonic acid group (PO_3H_2)[8a] and to the phosphonic acid bonded[10] to silicon atoms[10d] $(O{=}P(OSi)_2)$. Indeed, the ^{31}P NMR signal of a phosphonic acid bonded to a metal or a silicon atom[10d] is known to be shifted to higher field (about 10 ppm shift) than the signal of the parent free phosphonic acid.

CP MAS (Cross-polarisation magic angle spinning) ^{29}Si NMR of **XM-17.5Si** showed a signal M_1 at 12 ppm characteristic of $OSi(Me)_3$ units (Fig. 2). The Q_4 signal (−110 ppm) was the major one indicating that silanisation of

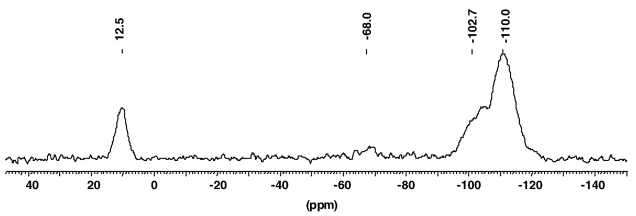


Fig. 2 CP MAS ^{29}Si NMR (79 MHz) of **XM-17.5**, after treatment by TMSBr and H_2O at RT.

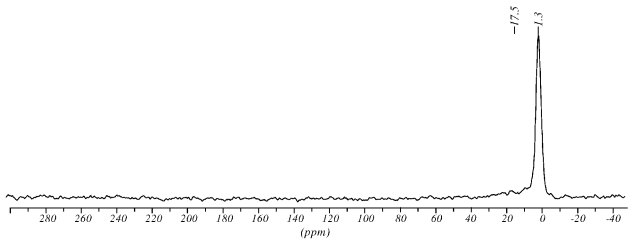
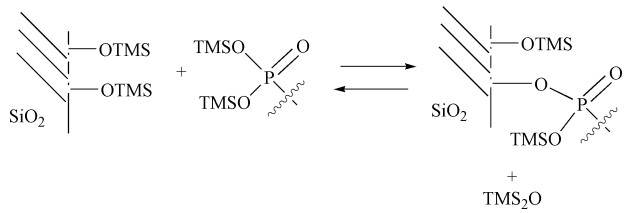


Fig. 3 CP MAS ^{13}C NMR (50 MHz) of **XM-17.5**, after treatment by TMSBr and H_2O at RT.



Scheme 2 Transesterification of the phosphonic groups by silica.

silica occurred. The T_3 unit (−68 ppm) was difficult to detect because of the low proportion of the organic part inside the solid.

CP MAS ^{13}C NMR (Fig. 3) showed only one major peak at 1.3 ppm, characteristic of the TMS group. Carbons of the backbone were not detected, and the ethoxy groups were not present which confirmed the cleavage.

Note that TMS groups bonded at the surface of silica are known to migrate[13] in the presence of water, and thus the bonded phosphonic acid groups could be linked to TMS or to silica.[10d] Transesterification of the phosphonic groups by silica could occur (Scheme 2).

As seen from the analyses, an important part of the phosphonic acids is not free. To liberate these functions, we then treated the material with H_2O in a sealed tube at 100 °C for 24 h. The material was then dried at 120 °C under vacuum overnight. HPDEC MAS ^{31}P NMR of **XM-17.5acid** showed a major change with a narrow signal at 32 ppm and the disappearance of the signal at 24.9 ppm (Fig. 4), in agreement with the free phosphonic acid group. The minor signal at 22.6 ppm corresponded to the residual phosphonic acids linked to silica or TMS group.

As can be seen from CP MAS ^{29}Si NMR spectra (Fig. 5), hydration of silica occurred, with cleavage of the TMS groups. The Q_3 and T_3 signals increased and the M_1 and Q_4 signals decreased.

CP MAS ^{13}C NMR (Fig. 6) confirmed the hydration of silica, as the intensity of the TMS group decreased. The carbon backbone was thus detected at 18 and 3 ppm, and ethoxy groups were not present.

Thus, simple treatment by water of our silanized co-gels is not sufficient to get the free phosphonic acid groups probably

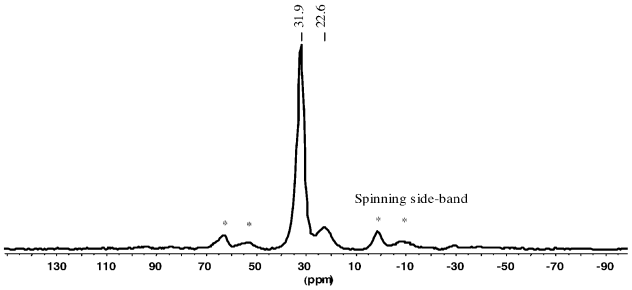


Fig. 4 HPDEC MAS ^{31}P NMR (80 MHz) of **XM-17.5** after treatment by TMSBr at 50 °C and H_2O at 120 °C.

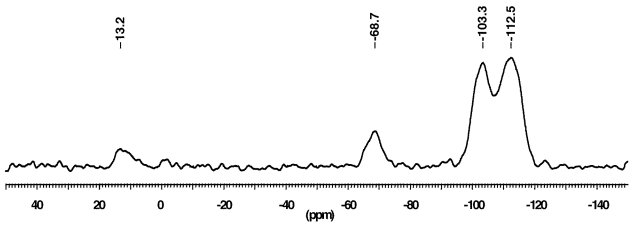


Fig. 5 CP MAS ^{29}Si NMR (79 MHz) of **XM-17.5**, after treatment by TMSBr and H_2O at 120 °C.

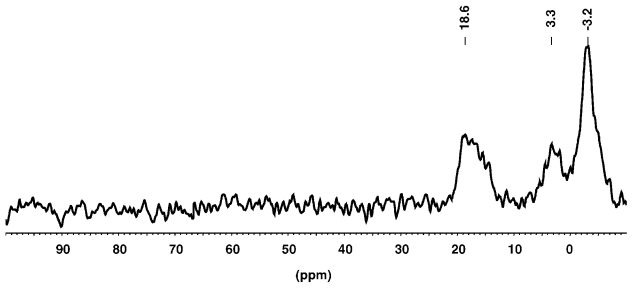


Fig. 6 CP MAS ^{13}C NMR (50 MHz) of **XM-17.5**, after treatment by TMSBr and H_2O at 120 °C.

because of their highly hydrophobic properties. Harsher conditions (100 °C sealed tube) had to be used. Note that the cleavage procedure worked for **XM-2** to **XM-17.5**, which showed that the reaction is general and does not depend on the texture of the solids (specific surface area increased from 5 to 488 $m^2\ g^{-1}$ by increasing x from 2 to 17.5).

The cleavage procedure was then applied to xerogels **X1a-X3** which possess a sensitive carbon backbone (Scheme 3).

Cleavage and hydrolysis of **X1a-10** (HPDEC MAS ^{31}P: 27.0 ppm) is representative. ^{31}P NMR spectra of compound **X1a-10acid** (Fig. 7) showed a signal at 23.7 ppm, corresponding to the free benzylic phosphonic acid, and a residual signal (shoulder) at 17 ppm corresponding to the bonded phosphonic acids.

^{13}C CP MAS NMR (Fig. 8) showed one signal at 129 ppm corresponding to the aromatics; signals of the ethoxy groups were not present any more and the signal of the residual TMS group was not detected.

To avoid esterification by silica, drying of the co-gels **X1a-X3** after hydrolysis was made under vacuum at RT. Fluorescence spectroscopy[9] confirmed the presence of the chromophore inside the solid. The chromophores were not damaged by the cleavage. Fluorescence spectra of solids **X1a-2**, **X1a-2Si**, and **X1a-2acid** are presented in Fig. 9.

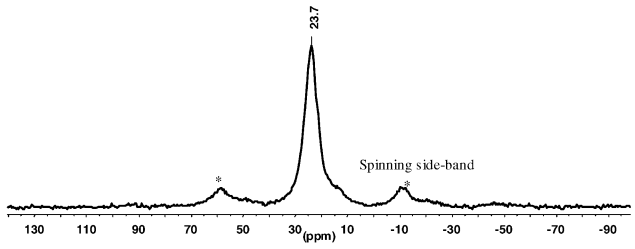


Fig. 7 HPDEC MAS ^{31}P NMR (80 MHz) of **X1a-10** after hydrolysis.

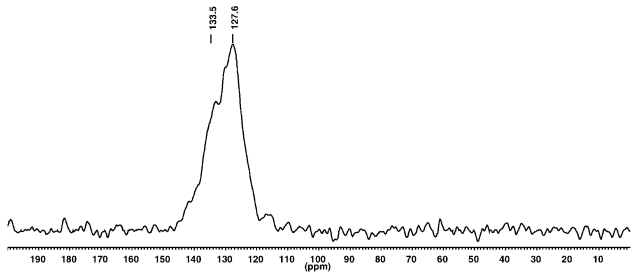


Fig. 8 CP MAS ^{13}C NMR (100 MHz) of **X1a-10acid**.

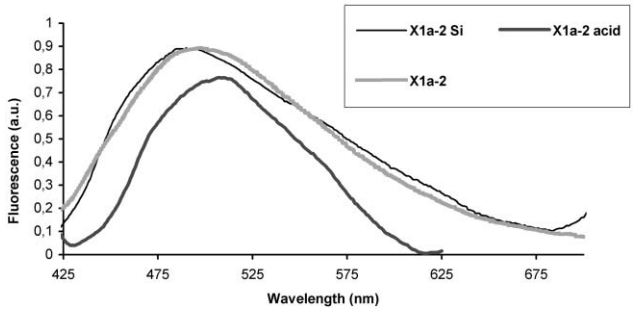


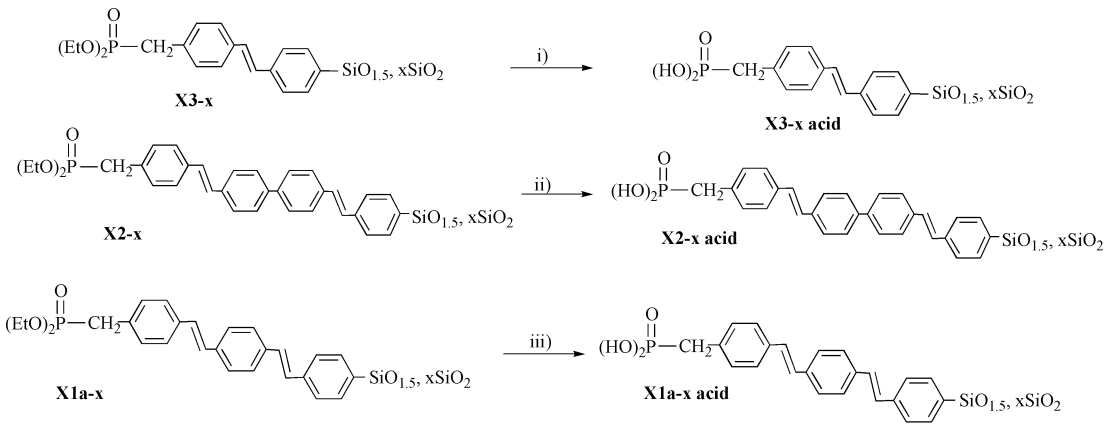
Fig. 9 Fluorescence of **X1a-2**, **X1a-2Si, X1a-2acid**.

The modification of the terminal group does not affect the fluorescence properties of the chromophore. The variations of the λ^{max}_{em} were not significant. This is confirmed with the emission spectra of **X2-5** and **X2-5acid** presented in Fig. 10 for which no variation of the λ^{max}_{em} was observed.

Thus, fluorescence was not affected by the cleavage.

Hydrolysis of the di-*tert*-butyl phosphonate ester of xerogels X1b

A di-*tert*-butyl phosphonate ester is known to be much more easier to cleave in acidic media than a diethyl phosphonate.[14a]



Scheme 3 Hydrolysis of the diethyl phosphonate ester of xerogels **X1a-X3**.

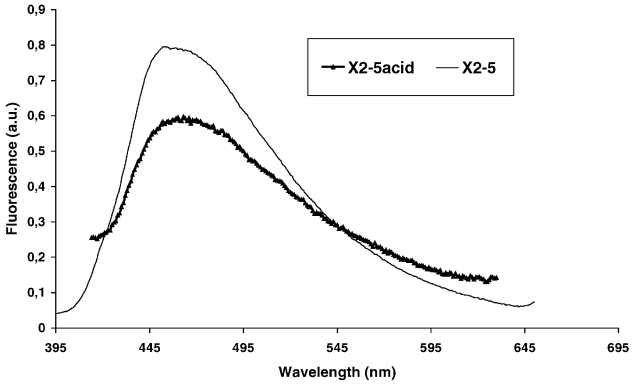


Fig. 10 Fluorescence of **X2-5** and **X2-5acid**.

Thus, the smooth conditions of cleavage are suitable for the syntheses of sensitive phosphotyrosyl peptide analogs.[14b] We have used that property to get the mildest conditions for hydrolysis of a phosphodiester in solids. Xerogels **X1b** possessing a di-*tert*-butyl phosphonate functionality and an arylene–vinylene backbone have been synthesized (Scheme 4).[9b]

Study of the di-*tert*-butyl ester cleavage of xerogel **X1b-5** (HPDEC MAS ^{31}P NMR: 17.0 ppm) is representative. When heated at 120 °C for 12 h under vacuum, HPDEC MAS ^{31}P NMR of xerogel **X1b-5** showed a new signal at 26 ppm characteristic of the free phosphonic acid (Fig. 11).

The same type of signal appeared four weeks after the syntheses of xerogels **X1b**, when stored at RT. A characteristic smell of isobutene evolved from the material. The *tert*-butyl phosphonate ester is thus readily cleaved in the presence of silica and is thus much less stable than an ethyl phosphonate ester. After treatment with HCl 1 M at 50 °C for two days, the free phosphonic acid (26.3 ppm) was obtained and the small signal at 17.9 ppm characteristic of the phosphonic acids bonded to silica was observed (Fig. 12). The cleavage was confirmed by ^{13}C NMR with the disappearance of the signal of the *tert*-butyl groups. The same spectrum as in Fig. 8 was observed. The chromophore was not damaged as analyzed by fluorescence spectroscopy.

Conclusion

We have described the hydrolysis of diethyl phosphonate esters covalently bonded to silica xerogels. TMSBr at 50 °C proved an efficient reagent to achieve the cleavage on materials possessing an aliphatic carbon chain and the procedure was smooth enough for sensitive materials possessing an arylene–vinylene carbon backbone. Hydration of silica at 100 °C was necessary to get the free phosphonic group. Fluorescence spectroscopy confirmed that the chromophore was not damaged. Alternatively, di-*tert*-butyl phosphonate ester was the precursor of choice to get free phosphonic acid groups under very mild conditions. Work is in progress to exploit the potential of our supported phosphonic acids and will be reported in due course.

Experimental

Manipulations of air-sensitive compounds were carried out under N_2 Solid-state NMR spectra were recorded using Bruker

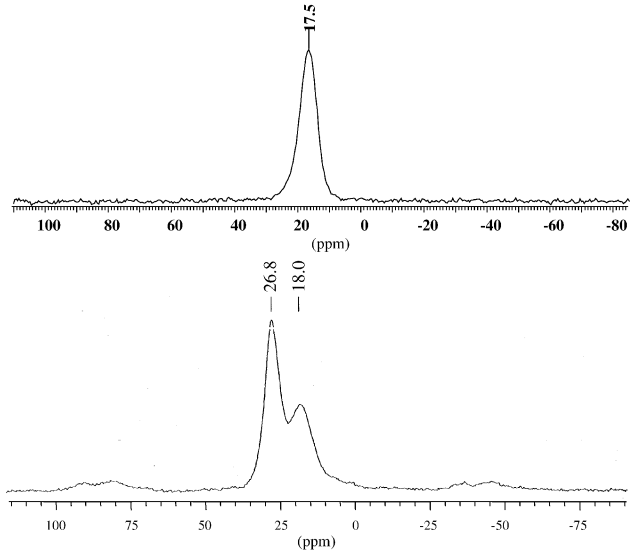


Fig. 11 HPDEC MAS ^{31}P NMR of **X1b-5** and **X1b-5** after heating under vacuum at 120 °C.

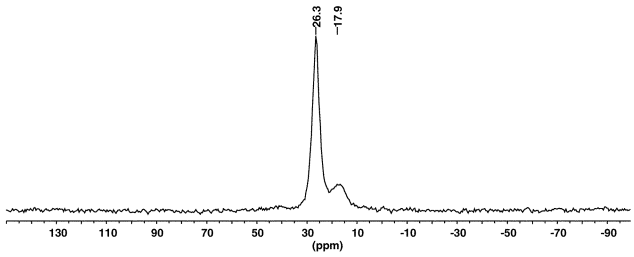
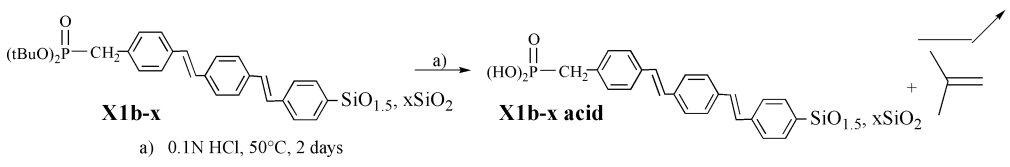


Fig. 12 HPDEC MAS ^{31}P NMR of xerogel **X1b-5** after treatment by HCl 1 M.

250, and 400 MHz spectrometers with a MAS 4 (spinning rate 9 kHz) or MAS 7 (spinning rate 3.5 kHz) probe. Contact time was 5 ms for CP MAS experiments and decoupling power was 200 W for HPDEC MAS experiments. Surface area measurements (BET) were recorded using a Micromeritics Gemini III 2375 under nitrogen atmosphere. Fluorescence was registered on a SLM Aminco 8100 spectrometer, by reflexion on a KBr Pellet. A front face sample holder was used and oriented at 60° in order to minimize the specular reflexion. Appropriate filters were used to eliminate Rayleigh and Raman scatters from the emission. (Diethoxyphosphorylethyl)triethoxysilane was purchased from ABCR.

Gelification of (diethoxyphosphorylethyl)triethoxysilane

(Diethoxyphosphorylethyl)triethoxysilane (1 g, 2.893 mmol) was dissolved in a mixture of EtOH–THF: 50 : 50. x equivalents of tetraethoxysilane (TEOS) were added. The concentration in Si derivatives was 0.5 M. $(1.5 + 2x)$ moles of H_2O were added. Then y% (y is the molar ratio calculated from the precursor) of NH_4F 0.25 M in water were added (see Table 1 for values of x and y). After gelification (7 days), the gels were powdered, and successively washed with EtOH, THF and



Scheme 4 Hydrolysis of the di-*tert*-butyl phosphonate ester of xerogels **X1b**.

Table 1 Gelation of precursor **XM**

XM	y NH_4F (%)	TEOS			H_2O/μL	Solvent EtOH–THF/mL
		x	Quantity/g	mmol		
XM-1	2	1	0.603	2.893	184	2 × 5.8
XM-2	3	2	1.206	5.186	290	2 × 8.7
XM-3	3	3	1.809	8.679	394	2 × 11.6
XM-4	2	4	2.412	11.572	447	2 × 14.5
XM-5	2	5	3.015	14.465	604	2 × 17.3
XM-10	2	10	6.030	28.930	1130	2 × 31.8
XM-15	2	15	9.045	43.395	1660	2 × 46.3
XM-17.5	2	17.5	10.553	50.628	1920	2 × 53.5
XM-20	2	20	12.060	57.860	2180	2 × 60.7

Table 2 Data for xerogels **XM**

XM	Solid-state MAS NMR (ppm)			Density/ g cm^{-3}	S_{BET}/ m^2 g^{-1}
	^{29}Si	^{31}P	^{13}C		
XM-1	−60.7 (T^2) −68.2 (T^3) −101.3 (Q^3) −110.5 (Q^4)	35.2		1.50	<5
XM-2	−60.9 (T^2) minor −67.3 (T^3) −100.7 (Q^3) −110.0 (Q^4)	—	3.9 16 63.2	1.53	<5
XM-3	—	—		1.69	
XM-4	—	—		1.67	17
XM-5	−67.6 (T^3) −91.6 (Q^2) minor −101.1 (Q^3) −109.6 (Q^4)	35.2	4.8 16 63.3	1.68	<5
XM-10	—	35.4	4.6 16.1 63.4		472
XM-15	—	35.3		1.88	421
XM-17.5	−66.4 (T^3) −91.6 (Q^2) minor −101.4 (Q^3) −109.8 (Q^4)	35.5		1.89	488
XM-20	—	35.6		1.90	587

acetone. Gels **XM** were dried at 120 °C under vacuum for 14 h. See Table 2 for data on the gels.

Hydrolysis of the diethyl phosphonate moiety of xerogel XM-17.5

0.50 g of the xerogel **XM-17.5** was suspended in 2.44 g of TMSBr (1.59×10^{-2} moles) under stirring at 50 °C for 24 h in a sealed tube. After evaporation of volatiles, the xerogel was suspended in water for 72 h at RT, filtered and dried under vacuum at 120 °C. ^{31}P NMR δ (ppm): 32.7, 24.9 (strong). ^{13}C NMR δ (ppm) 2.3 (CH_3-Si). ^{29}Si NMR δ (ppm) 12.5 (M^1), −103.7 (Q^3), −110.0 (Q^4) major. Density 2.22 g cm^{-3}. The xerogel was then treated in a sealed tube at 100 °C under stirring for 24 h, to hydrolyse the silyl ester intermediates. Filtration and drying under vacuum at RT afforded the supported free phosphonic acid. ^{31}P NMR δ (ppm): 32, 22.6 (minor). ^{13}C NMR δ (ppm) 18.6 (CH_2-P), 3.3 (CH_2-Si), −2 (CH_3-Si). ^{29}Si NMR δ (ppm) −68.1 (T^3), −103.7 (Q^3), −111.4 (Q^4). Density 2.34 g cm^{-3}.

The same procedure was applied to 0.5 g of xerogel **XM-2** and 9.186 g (60 mmol) of TMSBr at 70 °C. ^{31}P NMR δ (ppm): 32.1, 22.3 (minor). ^{13}C NMR δ (ppm): 18.8 (CH_2-P), 5.3 (CH_2-Si). Density 1.88 g cm^{-3}.

The same procedure was applied to 0.9 g of xerogel **XM-10** and 6.83 g (44.6 mmol) of TMSBr at 100 °C. ^{31}P NMR δ (ppm): 32.1, 22.3 (minor). ^{13}C NMR δ (ppm): 18.8 (CH_2-P), 5.3 (CH_2-Si). Density 1.93 g cm^{-3}.

The same procedure was applied to 0.2 g of xerogel **XM-5** and 2.36 g (15.6 mmol) of TMSBr at 120 °C. ^{31}P NMR δ (ppm): 33.1, 23.4 (minor). ^{13}C NMR δ (ppm): 18.2 (CH_2-P), 4.9 (CH_2-Si).

Hydrolysis of the diethyl phosphonate moiety of xerogel X3

0.30 g of the xerogel **X3-2** were suspended in 3.74 g of TMSBr (2.45×10^{-2} moles) under stirring at 100 °C for 24 h in a sealed tube. After evaporation of volatiles, the xerogel was then treated by water under stirring in a sealed tube at 100 °C for 24 h, to hydrolyse the silyl ester intermediates. Filtration and drying under vacuum at RT afforded the supported free phosphonic acid. ^{31}P NMR δ (ppm): 24.7. ^{13}C NMR δ (ppm): 129.4 (C arom.). Density 1.59 g cm^{-3}.

The same procedure was applied to 0.5 g of xerogel **X3-3** and 5.46 g (3.57×10^{-2} mol) of TMSBr. ^{31}P NMR δ (ppm): 26.1, 17.9 (minor). ^{13}C NMR δ (ppm): 128.7 (C arom.). Density 1.61 g cm^{-3}.

Hydrolysis of the diethyl phosphonate moiety of xerogel X2

The same procedure was applied to 0.18 g of xerogel **X2-5** and 3.75 g (8.59×10^{-3} mol) of TMSBr at 70 °C for 24 h. ^{31}P NMR δ (ppm): 25.6, 16.8 (minor). ^{13}C NMR δ (ppm): 136.0–127.9 (C arom.). Density 1.7 g cm^{-3}.

Hydrolysis of the diethyl phosphonate moiety of xerogel X1a

The same procedure was applied to 0.50 g of xerogel **X1a-2** and 5.15 g (3.36×10^{-2} mol) of TMSBr at 50 °C for 24 h. ^{31}P NMR δ (ppm): 23.7, 15.3 (minor). ^{13}C NMR δ (ppm): 135.6–127.7 (C arom.). Density 1.53 g cm^{-3}.

The same procedure was applied to 0.50 g of xerogel **X1a-10** and 5.8 g (3.79×10^{-2} mol) of TMSBr at 50 °C for 24 h. ^{31}P NMR δ (ppm): 24.8. ^{13}C NMR δ (ppm): 135.7–127.7 (C arom.). Density 1.85 g cm^{-3}.

Hydrolysis of the *tert*-butyl phosphonate moiety of xerogels X1b

0.50 g of xerogel **X1b-5** was stirred in 5 mL of HCl 1 M, at 50 °C for 48 h. After filtration, the xerogel was dried under vacuum at RT. ^{31}P NMR δ (ppm): 27.9, 18.2 (minor). ^{13}C NMR δ (ppm): 136.0–128.4 (C arom.). ^{29}Si NMR δ (ppm) 68.6.0 (T^2), −78.0 (T^3), −92.0 (Q^2), −101.0 (Q^3), −109.4 (Q^4).

The same procedure was applied to 0.55 g of xerogel **X1b-9**. ^{31}P NMR δ (ppm): 28.4, 18.1 (minor). ^{13}C NMR δ (ppm): 135.8–128.0 (C arom.). ^{29}Si NMR δ (ppm) −67.9 (T^2), −78.6 (T^3), −92.0 (Q^2), −101.3 (Q^3), −109.6 (Q^4).

The same procedure was applied to 0.5 g of xerogel **X1b-12**. ^{31}P NMR δ (ppm): 26.3, 17.9 (minor). ^{13}C NMR δ (ppm): 134.7–128.4 (C arom.).

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