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Sol–gel process: influence of the temperature on the textural properties of organosilsesquioxane materials

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The hydrolytic sol–gel polymerization of a variety of molecular precursors, $(RO)_3Si–X–Si(OR)_3$ with different structural features, has been investigated varying the temperature from −20 to +110 °C. "Rigid" precursors (R = Me, X = 1,4-C_6H_4, ferrocene-1,1′-diyl), "semi-rigid" precursors (R = Me, X = CH_2CH_2-1,4-$C_6H_4CH_2CH_2$; R = Et, X = $CH_2CH_2CH{=}CHCH{=}CHCH_2CH_2$) and alkylene-bridged precursors [R = Me, X = $(CH_2)_6$, $(CH_2)_{10}$; R = Et, X = $(CH_2)_2$, $(CH_2)_{14}$] were studied. A molecular precursor containing three $Si(OMe)_3$ groups, 1,3,5-$(MeO)_3SiC_6H_3$, was also considered. The reactions were performed using ionic and non-ionic catalysts. The ionic ones were a nucleophile [tetrabutylammonium fluoride (TBAF)], an acid (HCl) and a base (NaOH), and the non-ionic ones were nucleophiles [dimethylaminopyridine (DMAP), *N*-methylimidazole (NMI)]. The solvent employed was THF. Reactions were studied in MeOH only with TBAF as catalyst. In all cases the temperature appeared to be a fundamental parameter and had a drastic influence on the specific surface area and the porosity of the resulting solids. Particularly at low temperatures (−20 to 0 °C), the solids were mainly microporous with a weak mesoporous contribution without narrow pore size distribution. At higher temperature (20 to +110 °C), the solids exhibited very high specific surface areas and were mesoporous with a narrow pore size distribution. The specific surface area, the porosity and the pore size were highly dependent on the temperature. This work came in our study on the kinetic control of the texture.

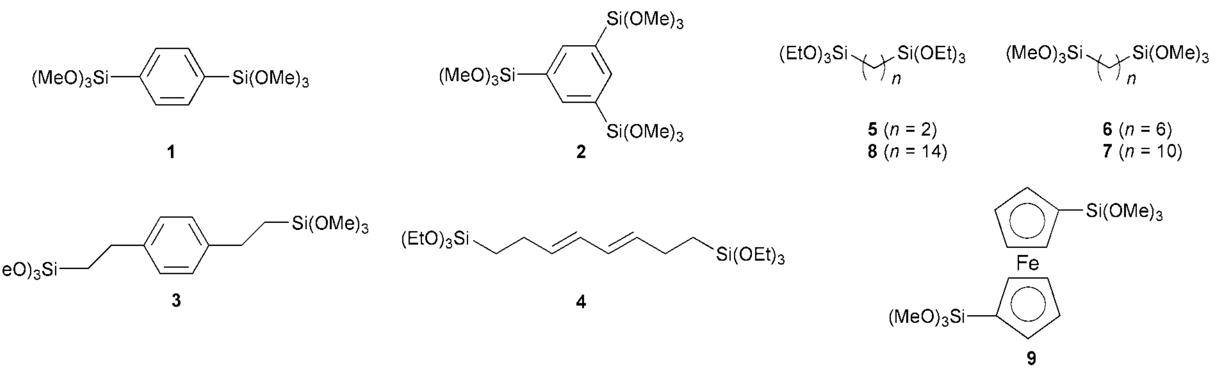
Introduction

The sol–gel process, offering unique possibilities for the elaboration of inorganic solids,[1] has recently proved to be of great interest for the preparation of both nanocomposite and nanostructured hybrid organic–inorganic materials.[2–7] In the case of nanostructured solids, the organic and inorganic units are covalently bound through at least two stable SiC bonds. We have previously reported that the macroscopic data describing the texture of xerogels (specific surface area, density, …) change with the parameters[8] governing the kinetics of polycondensation. They are highly dependant on the nature of the organic moieties,[9,10] the nature of the leaving group,[9] the solvent, the concentration of reagents[10] and the nature and concentration of catalyst.[11]

In this paper, we are focusing our interest on the influence of the temperature[12] on the level of condensation and the texture of resulting materials. We have chosen molecular precursors with different structural features (Scheme 1). Besides the linear rigid rod *p*-phenylene precursor **1** and a molecule presenting multiple condensation directions such as **2**, we considered more "flexible" molecules such as **3** and **4** bearing respectively an aromatic group (**3**) or a dienic system (**4**). We also studied precursors **5–8** presenting saturated aliphatic chains of different lengths. The case of ferrocene derivative **9** was also investigated. We report here results concerning the influence of varying the temperature from −20 to +110 °C on the textural properties of xerogels obtained with several kinds of catalysts: acid (HCl), base (NaOH), ionic nucleophile (TBAF) and non-ionic nucleophile (DMAP and NMI) in THF. MeOH was also used in some cases.

Experimental

Syntheses of precursors and preparation of the gels were carried out under argon using a vacuum line and Schlenk



Scheme 1 Molecular precursors.

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techniques.[13] Solvents and non-ionic catalysts were dried and distilled before use. Compounds **1**, **2**,[14] **4**,[15] **7**, **8**[16] and **9**[17] were prepared according to literature procedures, while **3**, **5** and **6** were commercially available and purified before use. The TBAF solution (1 mol l^{-1} in THF as measured by electrochemistry[18]), HCl solution (1 mol l^{-1} in H_2O) and NaOH solution (1 mol l^{-1} in H_2O) were commercially available. The HCl and NaOH solutions were titrated before used.

Solid state CP MAS NMR spectra were obtained with a Bruker FT AM 300 spectrometer: ^{13}C CP MAS NMR at 75.47 MHz, recycling delay 5 s and contact time 5 ms; ^{29}Si CP MAS NMR at 59.62 MHz, recycling delay 10 s and contact time 2 ms. The spinning rate was 5000 Hz in all cases. Chemical shifts are given relative to tetramethylsilane.

Specific surface areas, pore volumes and pore size distributions were determined using a Micromeritics Gemini III 2375 apparatus. The density of the materials was determined by a pycnometry measurement with helium: Micromeritics Accupyc 1330 apparatus.

Affinity of xerogels for water ($E_{0.6}$) was calculated by measurement of weight increases of solid in a 60% humidity atmosphere at 25 °C. This atmosphere is obtained with a saturated NaBr solution under vacuum.

Preparation of silsesquioxane gels

The preparation of gels was carried out according to the following general procedure. The preparation of xerogel **1TTa** is given as an example. The entire experiment (addition of reagents, gelation and ageing) was performed at −20 °C. To 2.86 g (9 mmol) of **1** in 9 ml of THF was added at −20 °C a solution of 90 μl (90 μmol) of TBAF and 486 μl (27 mmol) of H_2O in 8.40 ml of THF. The mixture was kept at −20 °C and after 90 minutes a monolithic gel formed. After ageing for 6 days at −20 °C, the solid was collected, then ground and washed twice with ethanol, acetone and diethyl ether. The resulting solid was dried at 120 °C *in vacuo* for 3 hours yielding 1.70 g of a white powder (**1TTa**). When the reaction was carried out at +110 °C, the xerogels were prepared in sealed tubes. The reagents were added at room temperature. The mixture was then cooled in liquid nitrogen and oxygen evacuated under vacuum. The tube was sealed, warmed up to room temperature and then put in an oven heated at +110 °C.

The experimental conditions for the xerogels obtained from **1–9** are reported in Tables 1–4.

Results and discussion

Preparation and spectroscopic characterization of xerogels

The solids were prepared by hydrolytic polycondensation of molecular precursors containing two $Si(OMe)_3$ or $Si(OEt)_3$ groups covalently bound to an organic unit (Scheme 2). Several types of organic spacers with different geometries have been investigated: "rigid" ones (**1** and **9**), more "flexible" ones presenting an unsaturated group (**3** and **4**), α,ω-bis(trialkoxysilyl)alkanes (**5–8**) and a molecule bearing three $Si(OMe)_3$ groups (**2**). The concentration of the precursor was 0.5 mol l^{-1} and the amount of catalyst was 1 mol% in all cases. Two kinds of catalysts were used: ionic catalysts [HCl, NaOH and tetrabutylammonium fluoride (TBAF)] and non-ionic catalysts [dimethylaminopyridine (DMAP) and *N*-methylimidazole (NMI)] using THF as solvent in the case of **1** and **3**. When the solvent was MeOH, only TBAF has been used in all cases. Ionic catalysts TBAF, HCl and NaOH were used in the case of **7**.

Considering the identification of the solids at the 'molecular level', the ^{13}C and ^{29}Si CP MAS NMR spectra gave confirmation that no SiC bond had been cleaved during the polycondensation.[19] In all cases, the ^{13}C CP MAS spectra showed the presence of the organic fragment, since the resonances due to the organic group were detected in the spectra. In addition the signals corresponding to residual methoxy or ethoxy groups were observed at δ 50 and δ 18 and 58, respectively. In the ^{29}Si CP MAS NMR spectra, no signal corresponding to Q units in the range δ −90 to −110 was observed in any spectrum. Furthermore, ^{29}Si CP MAS NMR provided information about the degree of polycondensation of the silsesquioxane network. CP MAS spectroscopy is not quantitative. However, it has been shown that single pulse experiments did not reveal any significant variation in relative peak intensity from the CP MAS spectra in the cases of **1** and **3**[10] and of alkylene bridged silsesquioxanes.[16] Thus the percentage of the different substructures was estimated *via* deconvolution of spectra. The values obtained for the different xerogels are reported in Tables 1–4. They reflect the order of magnitude of polycondensation at silicon.

Xerogels obtained from 1, 2 and 9. In the cases of **1** and **2**, where the organic precursor was 'rigid', the xerogels obtained exhibited similar ^{29}Si CP MAS NMR data: T^1 [C-$Si(OR)_2$-(OSi), δ −62.0], T^2 [C-Si(OR)$(OSi)_2$, δ −69.5] and T^3 [C-

Table 1 Experimental conditions and textural characteristics of xerogels obtained from **1**

Xerogel	Solvent	Catalyst	T/°C	Specific surface area/m^2 g^{-1}	Micropores (%)	Mesopore size/Å	Density/ g cm^{-3}	$E_{0.6}$ (%)	Level of condensation (%)
1TTa	THF	TBAF	−20	900	55	20–120[a]	1.42	27	71
1TTb	THF	TBAF	0	1150	40	20–120[a]	1.47	30	69
1TTc	THF	TBAF	+20	1300	10	20–120[a]	1.47	27	67
1TTd	THF	TBAF	+55	1300	5	55	1.45	17	74
1TTe	THF	TBAF	+110	1230	5	45	1.45	9	76
1TAa	THF	HCl	−20	<10	—	—	1.42	17	66
1TAb	THF	HCl	+20	540	80	20–120[a]	—	27	64
1TAc	THF	HCl	+55	460	80	20–120[a]	1.42	22	66
1TBa	THF	NaOH	−20	[b]	[b]	[b]	[b]	[b]	[b]
1TBb	THF	NaOH	+20	530	75	20–120[a]	—	20	62
1TBc	THF	NaOH	+55	300	55	20–120[a]	1.43	17	65
1TDa	THF	DMAP	−20	<10	—	—	1.36	9	58
1TDb	THF	DMAP	+30	680	65	20–70[a]	1.38	19	64
1TDc	THF	DMAP	+55	580	55	20–120[a]	1.33	9	62
1TNa	THF	NMI	+30	<10	—	—	1.39	9	60
1TNb	THF	NMI	+55	580	60	20–60[a]	1.39	16	62
1MTa	MeOH	TBAF	−20	420	50	20–120[a]	1.38	15	59
1MTb	MeOH	TBAF	+20	550	60	35	—	22	66
1MTc	MeOH	TBAF	+55	940	30	20–50[a]	1.38	17	70
1MTd	MeOH	TBAF	+110	890	10	20–120[a]	1.52	5	70

[a] No narrow pore size distribution. [b] No gel after several months.

Table 2 Experimental conditions and textural characteristics of xerogels obtained from **2** and **9** with 1 mol% of TBAF

Xerogel	Solvent	T/°C	Specific surface area/m^2 g^{-1}	Micropores (%)	Mesopore size/Å	Density/g cm^{-3}	$E_{0.6}$ (%)	Level of condensation (%)
2TTa	THF	−20	200	60	20–50[a]	2.02	11	62
2TTb	THF	0	600	40	20–70[a]	2.19	28	63
2TTc	THF	+20	760	10	20–120[a]	—	30	64
2TTd	THF	+55	800	0	20–110[a]	2.29	17	63
2TTe	THF	+110	1090	0	110	1.75	13	71
2MTa	MeOH	−20	470	20	20–70[a]	1.82	11	64
2MTb	MeOH	+20	770	10	20–120[a]	—	23	61
2MTc	MeOH	+55	1220	5	50–90	2.05	40	70
2MTd	MeOH	+110	950	0	105	1.65	6	68
9TTa	THF	−20	< 10	—	—	1.66	4	[b]
9TTb	THF	+20	25	30	20–120[a]	1.70	4	[b]
9TTc	THF	+55	275	40	20–120[a]	1.74	5	[b]
9TTd	THF	+110	385	35	20–50[a]	1.74	3	[b]

[a]No narrow pore size distribution. [b]Broad signal.

Si(OSi)$_3$, δ −78.0] substructures. Whatever the temperature, the catalyst or the solvent, similar degrees of condensation were obtained ranging between 60 and 70%. However in THF with TBAF, the xerogels **1TTa–1TTe** obtained from **1** were more polycondensed (67–71%). In the case of the ferrocene precursor **9**, the xerogels **9TTa–9TTd** exhibited a broad signal centered at δ −65; the level of condensation could not be determined.

Xerogels obtained from 3 and 4. When the precursor was more 'flexible' **3**, the degree of condensation depended on the solvent and the nature of the catalyst.[10,12] In THF, only T^2 (δ −58.0) and T^3 (δ −67.5) substructures were observed with TBAF and the degree of condensation ranged between 80 and 87%. In the case of ionic catalysts HCl and NaOH, T^1 (δ −49.5) units were also detected and the level of condensation ranged between 70–83% whereas it was around 66% with non-ionic catalysts and some T^0 (δ −42.5) units were observed. In MeOH with TBAF, the xerogels obtained from **3** were polycondensed in the range 61 and 73%, and the level of condensation increased with the temperature. In the case of precursor **4** containing a dienic system, the degree of condensation of the resulting xerogels depended on the temperature and increased from 81% at −20 °C (**4TTa**) to 93% at +110 °C (**4TTd**).

Xerogels obtained from 5–8. In the case of the 1,2-bis(triethoxysilyl)ethane **5**, the degree of condensation could not be evaluated since a broad signal was obtained. With the other α,ω-bis(trialkoxysilyl)alkanes **6** and **7**, high levels of condensation were observed in the range 74–92% with TBAF as catalyst. In the case of **7** no gel were obtained after several months whatever the temperature with NaOH and the xerogels **7TAa–7TAc** obtained using HCl as catalyst were moderately polycondensed (60–64%). In the case of **8**, where the aliphatic chain contains 14 carbon atoms, the solids were highly polycondensed and the level of condensation varied from 85% at −20 °C (**8TTa**) to 97% at +55 °C (**8TTc**).

These results show that the level of condensation for xerogels mainly depended on the nature of the organic group, the catalyst and the solvent. The lowest degrees of condensation were obtained with the more "rigid" precursors **1** and **2**, and in the case of alkylene-bridged polysilsesquioxanes, the condensation increased as the length of the aliphatic chain increased. In all cases, whatever the organic unit, higher degrees of condensation were obtained using TBAF in THF. When the solvent was methanol, the condensation generally decreased (case of **1** and **3**). *A minor effect of the temperature on the level of condensation for the different xerogels was shown.*

Textural properties of xerogels

Xerogels obtained from 1, 2 and 9. The textural properties (hydrophilic character, specific surface area, porosity and density) are reported in Tables 1 and 2.

Table 3 Experimental conditions and textural characteristics of xerogels obtained from **3** and **4**

Xerogel	Solvent	Catalyst	T/°C	Specific surface area/m^{2}g^{-1}	Micropores (%)	Mesopore size/Å	Density/g cm^{-3}	$E_{0.6}$ (%)	Level of condensation (%)
3TTa	THF	TBAF	−20	<10	—	—	1.30	7	82
3TTb	THF	TBAF	0	165	30	20–120[a]	1.31	8	—
3TTc	THF	TBAF	+20	565	25	20–120[a]	—	5	87
3TTd	THF	TBAF	+55	700	5	40	1.33	2	80
3TTe	THF	TBAF	+110	780	0	100	1.32	2	81
3TAa	THF	HCl	+20	<10	—	—	—	4	73
3TAb	THF	HCl	+55	<10	—	—	1.29	6	73
3TBa	THF	NaOH	+20	<10	—	—	—	2	83
3TBb	THF	NaOH	+55	<10	—	—	1.29	8	70
3TDa	THF	DMAP	+30	<10	—	—	1.27	9	67
3TDb	THF	DMAP	+55	<10	—	—	1.28	7	68
3TNa	THF	NMI	+30	<10	—	—	1.29	7	64
3TNb	THF	NMI	+55	<10	—	—	1.28	2	68
3MTa	MeOH	TBAF	+20	<10	—	—	—	2	61
3MTb	MeOH	TBAF	+55	<10	—	—	1.35	2	72
3MTc	MeOH	TBAF	+110	<10	—	—	1.29	2	73
4TTa	THF	TBAF	−20	250	20	20–50[a]	1.25	5	81
4TTb	THF	TBAF	+20	665	10	20–60[a]	1.27	3	86
4TTc	THF	TBAF	+55	870	5	35+60	1.27	1	91
4TTd	THF	TBAF	+110	910	0	35+55+80	1.26	1	93

[a]No narrow pore size distribution.

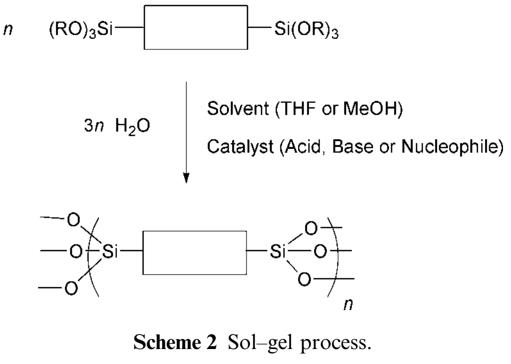
Table 4 Experimental conditions and textural characteristics of xerogels obtained from **5**, **6**, **7** and **8**

Xerogel	Solvent	Catalyst	T/°C	Specific surface area/m^2 g^{-1})	Micropores (%)	Mesopore size/Å	Density/g cm^{-3}	$E_{0.6}$ (%)	Level of condensation (%)
5TTa	THF	TBAF	−20	675	55	20–120[a]	1.55	21	[b]
5TTb	THF	TBAF	+20	795	60	20–120[a]	1.56	23	[b]
5TTc	THF	TBAF	+55	590	40	20–120[a]	1.46	5	[b]
6TTa	THF	TBAF	−20	<10	—	—	1.28	2	74
6TTb	THF	TBAF	+20	520	25	20–80[a]	1.29	2	80
6TTc	THF	TBAF	+55	570	0	20–80[a]	1.23	1	76
7TTa	THF	TBAF	−20	<10	—	—	1.15	1	77
7TTb	THF	TBAF	+20	290	5	20–70[a]	1.17	2	91
7TTc	THF	TBAF	+55	<10	—	—	1.16	1	88
7TTd	THF	TBAF	+110	<10	—	—	1.15	1	89
7TAa	THF	HCl	−20	<10	—	—	1.17	2	60
7TAb	THF	HCl	+20	<10	—	—	1.16	2	64
7TAc	THF	HCl	+55	<10	—	—	1.12	2	64
7TBa	THF	NaOH	−20	[c]	[c]	[c]	[c]	[c]	[c]
7TBb	THF	NaOH	+20	[c]	[c]	[c]	[c]	[c]	[c]
7TBc	THF	NaOH	+55	[c]	[c]	[c]	[c]	[c]	[c]
8TTa	THF	TBAF	−20	<10	—	—	1.09	1	85
8TTb	THF	TBAF	+20	<10	—	—	1.10	1	95
8TTc	THF	TBAF	+55	<10	—	—	1.10	1	97

[a]No narrow pore size distribution. [b]Broad signal. [c]No gel after several months.

Hydrophilic character. All the solids obtained from **1** exhibited a moderate to high affinity for water ($E_{0.6}$). Weight increases in a 60% humidity atmosphere at 25 °C varied from 10 to 30%. As previously shown, the hydrophilicity of xerogels obtained with ionic catalysts was higher than with non-ionic ones.[12] With TBAF, HCl or NaOH catalysts, the values were above 20% (20–30%), whereas with DMAP and NMI catalysts, the values obtained ranged between 10 and 20%. However, with all catalysts the main tendency was that $E_{0.6}$ decreased when the temperature of reaction increased, corresponding to a decrease of residual hydroxy groups at the surface of the materials. The lowest hydrophilicity was observed when the gels were prepared at +110 °C; $E_{0.6}$ was 9% for **1TTe** and 5% for **1MTd**. This fact is in agreement with the IR data of the xerogels: the ν(OH) absorption band centered at 3370 cm^{-1} due to the presence of silanol groups was more or less strong. The gels obtained from the ferrocene precursor **9** were hydrophobic in all cases; the affinity for water ranged between 3 and 5% (Table 2). The hydrophilicity of the solids obtained from **2** with TBAF was moderate to high: 11–40%. In THF at −20 °C (**2TTa**) and at +55 °C (**2TTd**), the values were lower (11 and 17%, respectively) than at 0 °C (**2TTb**) and +20 °C (**2TTc**) (28 and 30% respectively). In MeOH, the hydrophilicity ($E_{0.6}$) increased with the temperature. >From −20 to +55 °C, values changed from 11 to 40% (Table 2). When the hydrolysis was performed at +110 °C, the solids were more hydrophobic (13% for **2TTe** and 6% for **2MTd**).

BET measurements and porosity. The specific surface areas of the xerogels were determined. Thirty-five point adsorption–desorption isotherm plot measurements were used.[20] The specific surface areas were evaluated using the BET equation.[21] Determination of the porous volume by the BJH method[22,23] and evaluation of the microporous volume by the analysis of the t-plot diagram were performed in each case. Considering **1** with TBAF catalyst, values of specific surface areas were very high in THF (900–1300 m^2 g^{-1}), while in MeOH, they lay in the range 420–940 m^2 g^{-1}. The values increased with temperature in both solvents. The main influence of the temperature was observed on the porosity of the gels. When **1** was hydrolyzed in THF in the presence of TBAF, the shape of the curves of the adsorption–desorption isotherms depended strongly on the temperature. At low temperature (−20 to 0 °C) (**1TTa** and **1TTb**), the isotherm was of type I, indicating a largely microporous solid with a low mesoporous contribution, although vestiges of the hysteresis loop characteristic of capillary filling of mesopores were evident.[24] The microporous volume represented 40–55% of the total porous volume. The mesopore exhibited no narrow pore size distribution (20–120 Å). When the temperature was +20 °C (**1TTc**), the isotherm became characteristic of type IV.[24] The microporous volume was 10% and the mesopore size ranged between 20 and 120 Å. At +55 °C (**1TTd**), only 5% of micropores were present and mesopores showed a narrow pore size distribution (55–70 Å) characteristic of isotherms of type IV.[24] When the temperature was +110 °C, the pore size was 45 Å (**1TTe**). Similar behavior was observed when the solvent was MeOH. At +20 °C (**1MTb**) and +55 °C (**1MTc**), the distribution of the size of the mesopores was narrow (35 and 20–50 Å, respectively) (Table 1). With the other catalysts (HCl, NaOH, DMAP and NMI) in THF, values of specific surface areas were more moderate (300–700 m^2 g^{-1}). Surprisingly, with NaOH (**1TBa**) at −20 °C, no gel was formed after several months, and with HCl (**1TAa**), DMAP (**1TDa**) and NMI (**1TNa**) at −20 °C, no significant specific surface area (<10 m^2 g^{-1}) was observed (Table 1). In all other cases, the solids were mainly microporous, the microporous volume being 55–80% of the total porous volume. Only for DMAP at +30 °C (**1TDb**) and for NMI at +55 °C (**1TNb**) was a narrow pore size distribution was observed: 20–70 and 20–60 Å, respectively. The specific surface areas of the xerogels obtained from **2** with TBAF in THF and in MeOH followed the same tendency as that observed for the gels obtained from **1**. In THF at −20 °C (**2TTa**), the specific surface area was lower (200 m^2 g^{-1}) and the shape of the curve of the isotherms of N$_2$ adsorption–desorption (Fig. 1 – curve a) was characteristic of a microporous solid with a low mesoporous contribution. The microporous volume was 60%. When the temperature



Scheme 2 Sol–gel process.

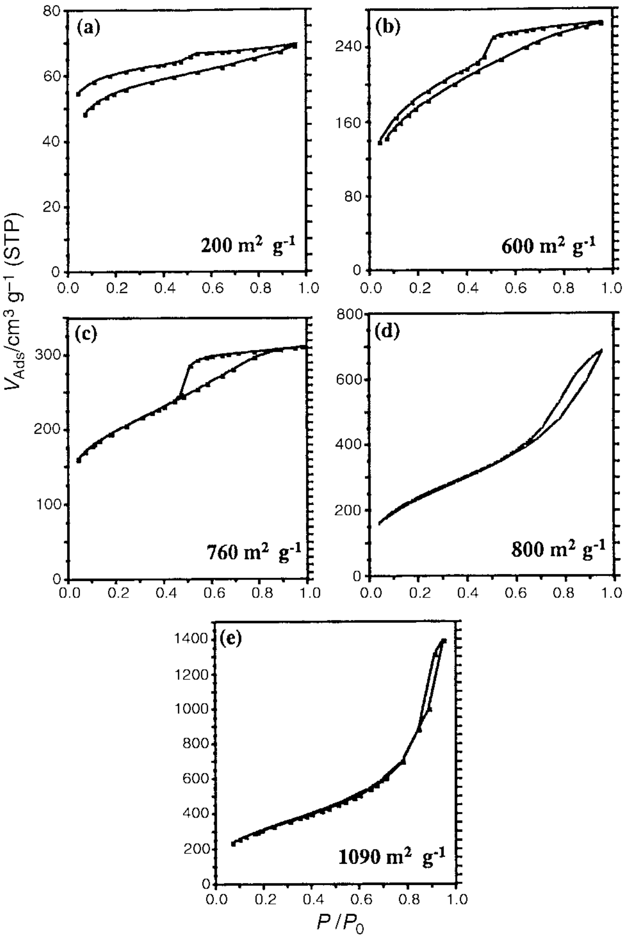


Fig. 1 N_2 adsorption–desorption isotherms of xerogels obtained from **2** in THF with TBAF: (a) **2TTa** (−20 °C), (b) **2TTb** (0 °C), (c) **2TTc** (+20 °C), (d) **2TTd** (+55 °C) and (e) **2TTe** (+110 °C).

increased, the specific surface area increased and the microporous contribution decreased. At +55 °C (**2TTd**) (Fig. 1 – curve d), the solid was mesoporous (Table 2). A narrow pore size distribution (110 Å) was observed only for the xerogel obtained at +110 °C (**2TTe**) (Fig. 1 – curve e). In MeOH, specific surface areas were higher than in THF (470–1220 $m^2 g^{-1}$) and they increased with temperature (Table 2). In all cases, the solids were mainly mesoporous. The volume of micropores was only 20% at −20 °C. In the same way, the xerogel **1MTd** prepared at +110 °C was mesoporous and the pore size was 105 Å. In the case of xerogels obtained from **9**, the specific surface areas of the solids appeared strongly dependent on the temperature. No significant specific surface area was observed at −20 °C for **9TTa** and it increased from 25 $m^2 g^{-1}$ (**9TTb**) at +20 °C to 385 $m^2 g^{-1}$ (**9TTd**) at +110 °C. The solids were microporous with a mesoporous contribution, the microporous volume lying in the range 30–40%. At +110 °C, the pore size distribution was narrower than at the other temperatures.

Densities. The densities of the gels obtained from **1** (Table 1) ranged between 1.33 and 1.52 $g cm^{-3}$. In the case of ionic catalysts in THF, the densities appeared slightly higher (1.41–1.47 $g cm^{-3}$) than in the case of non-ionic catalysts in THF (1.33–1.39 $g cm^{-3}$) and in the case of TBAF catalyst in MeOH (1.38 $g cm^{-3}$). This difference could be explained by a different distribution of the residual hydroxy or alkoxy groups within the hybrid network.[12] The temperature did not modify drastically the density of the xerogels obtained from **1**. The densities of the gels obtained from **2** were higher than those observed with **1**. They increased from 2.02 $g cm^{-3}$ (**2TTa**) to 2.29 $g cm^{-3}$ (**2TTd**) when the temperature varied from −20 to +55 °C in THF. Similar behavior was observed in MeOH (1.82 $g cm^{-3}$ for **2MTa** to 2.05 $g cm^{-3}$ for **2MTc**). The fact that higher densities were obtained for **2** might be due to the presence of nine directions for polycondensation for **2** instead of six for **1**. The functionalities around the silicon atoms were respectively $f = 6$ for **1** and $f = 9$ for **2**. It has been shown that this plays an important role in controlling the accessibility of organic groups to chemical reagents[10,25]. Furthermore the average number N of Si–O–Si bonds attached to each organic unit depends on the degree of condensation of the polysilsesquioxane network and on f. Thus the solids obtained from **2** appeared as more cross-linked materials in which the packing of the organic units is more dense. When the xerogels were prepared at +110 °C, lower densities were obtained for **2TTe** and **2MTd**, respectively: 1.75 and 1.65 $g cm^{-3}$. In this case, the reactions were performed in sealed tubes, and other physical parameters, especially the pressure, were involved in the process. They appeared to have an important influence on the density of the xerogels obtained from **2**.

Xerogels obtained from 3 and 4. The affinity for water of all xerogels obtained from **3** and **4** was very low, between 2 and 9% for **3** and 1 and 5% for **4** (Table 3). The solids were highly hydrophobic.

In most cases, starting from **3** no significant specific surface area was observed (< 10 $m^2 g^{-1}$) (Table 3). However, when the hydrolysis polycondensation was performed in THF in the presence of TBAF, the temperature had a drastic influence on the specific surface area and the porosity of the resulting solids. At −20 °C (**3TTa**) the gels exhibited no specific surface area. At 0 °C (**3TTb**), a moderate surface was observed: 165 $m^2 g^{-1}$. When the temperature increased, the specific surface areas increased; at +20 °C (**3TTc**) and +55 °C (**3TTd**), the values were respectively 565 and 700 $m^2 g^{-1}$. The solids obtained at 0 °C (**3TTb**) and +20 °C (**3TTc**) were mainly mesoporous with microporous volumes of 30 and 25% respectively, without narrow pore size distribution. At +55 °C (**3TTd**), the volume of micropores represented only 5% of the total porous volume. The mesopores exhibited a narrow pore size distribution of 40 Å (Table 3). When the reaction was performed at +110 °C, a mesoporous solid (**3TTe**) formed and the pore size was 100 Å. The same behavior was observed for the hydrolysis polycondensation of **4** in THF with TBAF (Table 3). The specific surface area increased with the temperature, while the solids became mesoporous with a narrow pore size distribution (Table 3).

The densities of the xerogels obtained from **3** ranged between 1.27 and 1.35 $g cm^{-3}$. They were lower than those of xerogels obtained from **1** or **2**. This result could be expected since the volume occupied by the organic group is larger in the solids obtained from **3** than those obtained from **1** or **2** because of the possibilities of some conformational mobility.

Xerogels obtained from 5–8. The textural properties of these solids are reported in Table 4. The solvent was THF and TBAF was used as catalyst. The xerogels were hydrophobic in most cases; the affinity for water was very low (1–2%). In contrast, the solids **5TTa** and **5TTb** obtained from 1,2-bis(triethoxysilyl)ethane **5** at −20 and +20 °C appeared highly hydrophilic, whereas when **5TTc** was prepared at +55 °C, the weight increase was only 5%.

The specific surface areas of the xerogels depended strongly on the length of the alkylene spacer, as previously observed.[16] The ethylene-bridged xerogels derived from **5** possessed high specific surface areas whatever the temperature of reaction and were microporous with a mesoporous contribution. The microporous volume ranged between 40 and 60%, and the pore size varied from 20 to 120 Å. In the case of 1,6-bis(trimethoxysilyl)hexane **6**, no significant specific surface area was obtained at −20 °C (**6TTa**) while porous solids were observed at +20 °C (**6TTb**) and +55 °C (**6TTc**). The xerogel **6TTc** was mesoporous. With longer alkylene spacers, the precursors **7** and **8** led to non-porous materials with no significant specific surface area. Similar behavior has been reported.[16] In the case of 1,10-bis(trimethoxysilyl)decane **7**, no gel formed after several months when NaOH was used as catalyst. A porous xerogel formed in only one case: **7TTb** was prepared at +20 °C in THF in the presence of TBAF. The surface area was 290 $m^2 g^{-1}$.

The densities of xerogels obtained from **5–8** varied with the length of the alkylene bridge: the longer the bridge, the lower the density. The densities of xerogels **5TTa–5TTc** (two carbon atoms) ranged between 1.46 and 1.56 $g cm^{-3}$, the densities of **6TTa–6TTc** (six carbon atoms) lay in the range 1.23–1.28 $g cm^{-3}$ and the xerogels derived from **7** and **8** (ten and fourteen carbon atoms respectively) exhibited the lowest densities, in the range 1.09–1.17 $g cm^{-3}$.

The surface areas and porosities of bridged polysilsesquioxane xerogels appeared highly dependent on both the structural rigidity of the bridging group and the temperature. In the case of the longer alkylene bridging groups (**7**, **8** with a number of carbon atoms > 6) highly polycondensed xerogels formed, certainly leading to compliant networks, such that collapse of porosity during drying readily occurred, as already observed.[26] On the other hand, "rigid" bridging groups **1**, **2** and **9** presumably inhibited the formation of small cyclic structures, and produced relatively noncompliant networks, inhibiting the collapse of porosity during drying.

Conclusion

The results presented here clearly show that the macroscopic properties (texture, specific surface area, porosity, density, …) of hybrid materials obtained by hydrolytic polycondensation are controlled by the experimental parameters of the reaction as previously reported.[8–12] In this paper, we investigated a variety of molecular precursors with three different structural features ("rigid", "semi-rigid" or "flexible" geometries) and the influence of the temperature on the properties of the resulting xerogels.

We have shown that the *level of condensation at silicon for xerogels mainly depended on the nature of the organic group*: for a given molecular precursor, the solvent, the catalyst and the temperature of the reaction had only a minor influence on the degree of condensation. The more "rigid" precursors led to the lowest levels of condensation whatever the catalyst, the solvent and the temperature (cases of **1** and **2**). In the case of "semi-rigid" precursor **3**, the highest degrees of condensation were obtained with ionic catalyst in THF whatever the temperature. When the molecular precursor contained a saturated aliphatic chain (**5–8**), the level of condensation increased with the length of the chain. *Varying the temperature from −20 to +110 °C did not change significantly the level of condensation of silicon atoms for a given molecular precursor, solvent and catalyst.*

In contrast, the temperature, as well as the other kinetic parameters, were fundamental for the textural properties of the solids (specific surface area, porosity, density). The solids prepared at low temperatures were mainly microporous with a mesoporous contribution and no narrow pore size distribution. Increasing the temperature of reaction led to the formation of mesoporous solids having higher specific surface areas and narrow pore size distributions.

The results presented here show that for a given molecular precursor the temperature is a fundamental parameter which allows the control of the textural properties of the solids and induces drastic changes in the porosity. In contrast, the degree of condensation remains largely insensitive to the temperature. These facts suggest that these two properties (level of condensation at silicon atoms and texture) are not controlled during the same steps of the sol–gel type synthesis: precursor →oligomers→polymers→colloids→sol→gel. The polycondensation at silicon atoms might be determined during the first steps of the process while the texture could be controlled during the gel formation. We report here a useful method (solvent THF, catalyst TBAF, temperature +110 °C) to obtain mesoporous organic–inorganic hybrid materials exhibiting high specific surface areas and presenting a narrow pore size distribution independently of the nature of the organic group.

References

1 C. J. Brinker and G. W. Scherer, *Sol-Gel Science*, Academic Press, London, 1990.
2 L. L. Hench and J. K. West, *Chem. Rev.*, 1990, **90**, 33.
3 D. A. Loy and K. J. Shea, *Chem. Rev.*, 1995, **95**, 1431 and references therein; S. T. Hobson and K. J. Shea, *Chem. Mater.*, 1997, **9**, 616.
4 P. Judeinstein and C. Sanchez, *J. Mater. Chem.*, 1996, **6**, 511; B. Lebeau, S. Brasselet, J. Zyss and C. Sanchez, *Chem. Mater.*, 1997, **9**, 1012.
5 U. Schübert, N. Hüsing and A. Lorenz, *Chem. Mater.*, 1995, **7**, 2010.
6 R. J. P. Corriu, *Polyhedron*, 1998, **17**, 925; G. Cerveau and R. J. P. Corriu, *Coord. Chem. Rev.*, 1998, **180 (part 2)**, 1051 and references therein; R. J. P. Corriu, *Angew. Chem.*, 2000, in press.
7 S. W. Carr, M. Motevalli, D. Li Ou and A. C. Sullivan, *J. Mater. Chem.*, 1997, **7**, 865.
8 G. Cerveau, R. J. P. Corriu and C. Fischmeister-Lepeytre, *J. Mater. Chem.*, 1999, **9**, 1149.
9 G. Cerveau, R. J. P. Corriu and C. Lepeytre, *J. Organomet. Chem.*, 1997, **548**, 99.
10 G. Cerveau, R. J. P. Corriu, C. Lepeytre and P. H. Mutin, *J. Mater. Chem.*, 1998, **8**, 2707.
11 G. Cerveau, R. J. P. Corriu and E. Framery, *Polyhedron*, 2000, in press.
12 G. Cerveau, R. J. P. Corriu and E. Framery, *Chem. Commun.*, 1999, 2080.
13 D. F. Schriver, *The manipulation of air-sensitive compounds*, MacGraw-Hill, New York, 1969.
14 R. J. P. Corriu, J. Moreau, P. Thépot and M. Wong Chi Man, *Chem. Mater.*, 1992, **4**, 1217.
15 G. Cerveau, R. J. P. Corriu and B. Dabiens, submitted for publication.
16 H. W. Oviatt Jr., K. J. Shea and J. H. Small, *Chem. Mater.*, 1993, **5**, 943.
17 G. Cerveau, C. Chuit, E. Colomer, R. J. P. Corriu and C. Reyé, *Organometallics*, 1990, **9**, 2415.
18 D. A. Skoog, D. M. West and F. J. Holler, *Fundamentals of analytical chemistry*, International Edition, Saunders College Publishing, 1992, p. 873.
19 M. Mägi, E. Lippmaa, A. Samoson, G. Engelhardt and A. R. Grimmer, *J. Phys. Chem.*, 1984, **88**, 1518; H. Marsmann, *^{29}Si NMR Spectroscopic Results*, ed. P. Diehl, E. Fluck and R. Kosfeld, Springer Verlag, Berlin, 1981.
20 S. J. Gregg and S. W. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, London, 1982.
21 S. Brunauer, P. H. Emmet and E. Teller, *J. Am. Chem. Soc.*, 1938, **60**, 309.
22 S. Brunauer, L. S. Deming, W. S. Deming and E. Teller, *J. Am. Chem. Soc.*, 1940, **62**, 1723.
23 E. Barett, L. Joyner and P. Halenda, *J. Am. Chem. Soc.*, 1951, **73**, 373.
24 K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquérol and T. Siemieniewska, *Pure Appl. Chem.*, 1985, **57**, 603.
25 J. P. Bezombes, C. Chuit, R. J. P. Corriu and C. Reyé, *J. Mater. Chem.*, 1999, **9**, 1727.
26 T. J. Barton, L. M. Bull, W. G. Klemperer, D. A. Loy, B. McEnaney, M. Misono, P. A. Monson, G. Pez, G. W. Scherer, J. C. Vartulli and O. M. Yaghi, *Chem. Mater.*, 1999, **11**, 2633.