

Sol-gel process—influence of ageing on the textural properties of organosilsesquioxane materials

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Received 17th October 2000, Accepted 13th December 2000

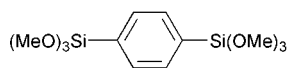
First published as an Advance Article on the web 22nd January 2001

The hydrolytic sol-gel polymerization of a variety of molecular precursors with a “rigid” geometry 1,4- $C_6H_4[Si(OMe)_3]_2$ **1** and a “flexible” geometry $(MeO)_3Si-(CH_2)_{10}-Si(OMe)_3$ **2** was investigated varying the nature of the catalyst, the temperature and the length of ageing. The reactions were performed using ionic and non-ionic catalysts. The ionic ones were a nucleophile [tetrabutylammonium fluoride (TBAF)] or acid (HCl) and the non-ionic one was dimethylaminopyridine (DMAP). The solvent was THF. In all cases, the length of ageing had a minor effect on the level of condensation at silicon atoms of the different xerogels. Only a small increase was observed. In contrast, the specific surface area, the porosity and the pore size were highly dependent on the length of ageing. The longer ageing times favoured the formation of mesoporous solids with high specific surface areas and narrow pore size distribution.

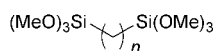
Introduction

Over the past few years, there has been growing interest in “Chimie Douce”,¹ and particularly in the elaboration of solids by the sol-gel process.^{2–7} This method allows the preparation of both nanocomposite and nanostructured hybrid organic-inorganic materials under smooth conditions.^{8–16} In the case of nanostructured hybrid materials, the molecular precursor undergoes an inorganic polymerization which leads to a highly crosslinked solid through a hydrolytic polycondensation.^{8,10,13,17,18} We have recently shown that the kinetic parameters involved during the hydrolytic process¹⁹ control the macroscopic data which describe the texture of xerogels: organic moiety,^{20,21} leaving group,²⁰ solvent,²⁰ catalyst,²² concentration^{21,22} and temperature.^{23,24} We have particularly shown that the nature of the organic group, “rigid” or “flexible”, has a drastic influence on the properties of the hybrid solids.^{20,21}

In this paper, we are focusing our interest on the influence of the ageing time on both the level of condensation and the textural properties of the resulting materials. We have chosen for this study two molecular precursors having different structural features: the linear “rigid” rod *p*-phenylene precursor **1** and the “flexible” one **2** presenting a saturated aliphatic long chain. We report here the results concerning the influence of varying the ageing time from 0 to 30 days for a given temperature of gelation on the properties of the xerogels obtained with different catalysts: ionic nucleophile (TBAF), acid (HCl) and non-ionic nucleophile (DMAP) in THF. Ageing was also performed at different temperatures.



1



2 ($n = 10$)

Experimental

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

techniques.²⁵ THF and DMAP were dried and distilled before use. Compounds **1**²⁶ and **2**²⁷ were prepared according to literature procedures. The TBAF solution (1 mol l^{-1} in THF as measured by electrochemistry²⁸), HCl solution (1 mol l^{-1} in H_2O) was commercial and was titrated before use.

Solid state CP MAS NMR spectra were obtained with a Bruker FT AM 300 spectrometer:²⁹Si CP MAS NMR at 59.62 MHz, recycling delay 10 s and contact time 5 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 distribution 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 **1TAb** is given as an example. The entire experiment (addition of reagents, gelation and ageing) was performed at -20°C . To 2.86 g (9 moles) of **1** in 9 ml of THF was added at -20°C a solution of 90 μl (90 μmoles) of TBAF and 486 μl (27 mmoles) 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 **1TAb**.

The experimental conditions, the textural characteristics and ²⁹Si NMR data for the xerogels obtained from **1** and **2** are reported in Tables 1 and 2.

Results and discussion

The two precursors **1** “rigid” and **2** “flexible” have been studied (Scheme 1). The hydrolysis was performed in THF, the

Table 1 Structural and textural characteristics of xerogels obtained from **1** in THF (0.5 M) with 1 mol% catalyst

Entry	Xerogel	Catalyst	Temp./°C		Ageing time/d	²⁹ Si NMR (%)					BET results		
			Gel ^a	Ageing		T ⁰	T ¹	T ²	T ³	LC ^b	SSA/m ² g ^{-1c}	Micropores (%) ^d	Size/Å ^e
1	1TAa	TBAF	-20	-20		0	16	49	35	73	700	55	20–70 ^f
2	1TAb				6	0	18	49	33	71	900	55	20–70 ^f
3	1TAc				15	0	24	32	44	73	940	45	20–80 ^f
4	1TAd				30	0	22	50	28	69	915	35	0–60 ^f
5	1TBa	TBAF	-20	+55	6	0	11	50	39	76	1385	5	50
6	1TCa	TBAF	+20	+20	0	0	18	55	27	70	940	30	20–60 ^f
7	1TCb				6	0	16	64	20	67	1300	10	20–120 ^f
8	1TCc				15	0	7	66	27	73	1370	5	20–80 ^f
9	1TCd				30	0	13	54	33	73	1430	5	45
10	1TCe				90	0	9	52	39	77	1385	5	20–50 ^f
11	1TDa	TBAF	+55	-20	6	0	19	44	37	73	1015	20	20–50 ^f
12	1TEa	TBAF	+55	+55	0	0	22	41	37	72	1135	15	20–60 ^f
13	1TEb				6	0	18	42	40	74	1300	5	65
14	1TEc				15	0	15	39	46	77	1290	0	65
15	1TEd				30	0	10	38	52	80	1270	0	50
16	1HAa	HCl	+20	+20	0	0	38	62	0	54	<10	—	—
17	1HAb				3	0	40	51	14	56	<10	—	—
18	1HAc				6	0	21	65	14	64	540	80	20–120 ^f
19	1HAd				15	0	31	51	18	62	185	65	20–120 ^f
20	1HAe				30	0	32	60	8	59	35	30	20–120 ^f
21	1DAa	DMAP	+30	+30	0	9	28	37	26	60	<10	—	—
22	1DAb				3	9	28	37	26	60	475	65	20–60 ^f
23	1DAc				6	5	30	34	31	64	680	65	20–70 ^f
24	1DAd				15	0	27	45	28	67	875	45	20–50 ^f
25	1DAe				30	0	21	49	30	70	1160	15	20–50 ^f

^aTemperature of gelation. ^bLevel of condensation. ^cSpecific surface area. ^dPercentage of micropores. ^eSize of mesopores. ^fNo narrow pore size distribution.

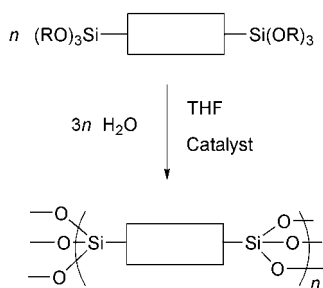
Table 2 Structural and textural characteristics of xerogels obtained from **2** in THF (0.5 M) with 1 mol% catalyst

Entry	Xerogel	Catalyst	Temp./°C		Ageing time/d	²⁹ Si NMR (%)					BET results		
			Gel ^a	Ageing		T ⁰	T ¹	T ²	T ³	LC ^b	SSA/m ² g ^{-1c}	Micropores (%) ^d	Size/Å ^e
1	2TAa	TBAF	+20	+20	0	5	1	28	66	85	<100	—	—
2	2TAb				6	0	0	27	73	91	290	5	20–70 ^f
3	2TAc				15	0	0	35	65	88	350	5	20–50 ^f
4	2TAd				30	0	0	27	73	91	410	0	45
5	2HAa	HCl	+20	+20	0	0	24	54	22	66	<100	—	—
6	2HAb				6	0	28	51	21	64	<100	—	—
7	2HAc				15	0	21	60	19	66	<100	—	—
8	2HAD				30	0	27	54	19	64	<100	—	—

^aTemperature of gelation. ^bLevel of condensation. ^cSpecific surface area. ^dPercentage of micropores. ^eSize of mesopores. ^fNo narrow pore size distribution.

concentration of the precursor was 0.5 mol l⁻¹ and the catalyst was 1 mol% in all cases. Three catalysts were used in the case of **1**: ionic ones (TBAF and HCl) and a non-ionic one (DMAP). Three temperatures were chosen for the whole process (gelation and ageing): -20 °C, +20 °C and +55 °C. In addition, when the catalyst was TBAF, gelation was performed at -20 °C and

ageing at +55 °C and conversely gelation at +55 °C and ageing at -20 °C. In the case of **2**, TBAF and HCl were used at +20 °C. All the xerogels obtained were analysed by ²⁹Si CP MAS NMR spectroscopy. The texture of the solids was studied by measuring specific surface area, pore size, density and hydrophilicity.

**Scheme 1** Sol-gel process.

Xerogels obtained from **1**

²⁹Si CP MAS NMR data. The ²⁹Si CP MAS NMR data of the xerogels obtained from **1** were very similar whatever the gelation and ageing conditions. When the catalyst was TBAF, the T¹ [C-Si(OR)₂(OSi), δ -62.0 ppm], T² [C-Si(OR)(OSi)₂, δ -69.5 ppm] and T³ [C-Si(OSi)₃, δ -78.0 ppm] substructures were observed in all cases. The percentages of the different substructures were estimated by deconvolution of the spectra, since it has been shown previously that single pulse experiments did not reveal any significant variation in relative peak intensity from the CP MAS spectra in the case of **1**.²¹ The values are

reported in Table 1.† When the gel was prepared at a given temperature, no drastic variations were observed for the percentages of the different T units when the length of ageing time increased. Thus the level of condensation at silicon atoms lay in the same range: at -20°C (xerogels **1TAa–1TAd**, Table 1, entries 1–4) and at $+20^{\circ}\text{C}$ (**1TCa–1TCe**, Table 1, entries 6–10) it was 69–73% and 67–77% respectively. When the whole process was performed at $+55^{\circ}\text{C}$, the degree of condensation appeared slightly higher (72–80%), and as normally expected the site populations of T^2 and T^3 increased when the T^1 decreased (**1TEa–1TEd**, Table 1, entries 12–15). A comparison between the xerogels **1TAa**, **1TBa**, **1TDa** and **1TEb** (Table 1, entries 2, 5, 11 and 13) which were prepared under different conditions and aged during the same time (6 days) showed only a minor influence of the ageing conditions on the ^{29}Si NMR data of the resulting solids (**1TAa** and **1TBa**: gel formation -20°C and ageing temperature -20°C and $+55^{\circ}\text{C}$ respectively; **1TDa** and **1TEb**: gel formation at $+55^{\circ}\text{C}$ and ageing temperature -20°C and $+55^{\circ}\text{C}$ respectively).

In the case of HCl catalysis, only T^1 and T^2 substructures were detected when no ageing of the gel was performed (**1HAa**, Table 1, entry 16) and the level of condensation at silicon atoms was low (54%). When the ageing time was increased, T^3 units appeared and the degree of condensation increased slightly.

In the case of the nucleophilic catalyst (DMAP), T^0 [$\text{C-Si}(\text{OR})_3$, $\delta -54.4$ ppm] substructures were detected for the shorter ageing times (**1DAa–1DAc**, Table 1, entries 21–23). The degree of condensation at silicon atoms ranged between 60% (**1DAa**) and 70% (**1DAe**).

Texture, density and hydrophilic character of the solids. The specific surface areas of the xerogels were determined. They are reported in Table 1. Thirty-five points from the adsorption–desorption isotherm plot measurements were used.³⁰ The specific surface areas were evaluated using the BET equation.³¹ The determination of the porous volume by the BJH method^{32,33} and the evaluation of the microporous volume by analysis of the t -plot diagram were achieved in each case.

With TBAF as catalyst, the specific surface areas were very high in all cases. The values lay in the range $700\text{--}1400\text{ m}^2\text{ g}^{-1}$. When the whole reaction was performed at -20°C (xerogels **1TAa–1TAd**, Table 1, entries 1–4) the shape of the curve of adsorption–desorption isotherms was the same whatever the ageing time (Fig. 1a). The isotherm was of type I, indicating a largely microporous solid with a low mesoporous contribution. The microporous volume represented 35–55% of the total porous volume and the mesopores exhibited no narrow pore size distribution ($20\text{--}80\text{ \AA}$). The specific surface area increased slightly when the ageing time was longer ($700\text{ m}^2\text{ g}^{-1}$ after 0 day, **1TAa**, to $915\text{ m}^2\text{ g}^{-1}$ after 30 days, **1TAd**, Table 1, entries 1 and 4). After ageing for 6 days, no influence was detected on the surface; however the microporous volume decreased from 55% to 35%. The mesopore size did not depend on the ageing time. When the hydrolytic process was performed at $+20^{\circ}\text{C}$, with TBAF catalyst, the same behavior was observed. After ageing 0 day (**1TCa**, Table 1, entry 6), the BET surface area was $940\text{ m}^2\text{ g}^{-1}$ and the microporous volume was 30% (isotherm type I). When the ageing time increased from 6 to 90 days, the specific surface area did not change significantly; only 5–10% of micropores were present. The shape of the isotherm became characteristic of type IV.^{34,35} The pore size distribution became narrower and for **1TCd** (Table 1, entry 9), the

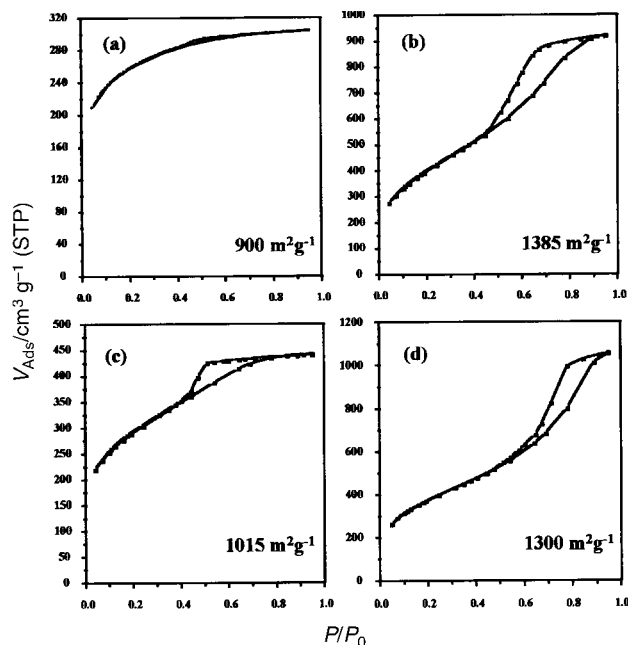


Fig. 1 N_2 adsorption–desorption isotherms of xerogels obtained from **1** in THF with TBAF after 6 days of ageing: a) **1TAa**, b) **1TBa**, c) **1TDa**, d) **1TEb**.

mesopore size was 45 \AA . Similar behavior was observed when the temperature of the whole reaction was $+55^{\circ}\text{C}$. Interestingly in this case, mesoporous solids with narrow pore size (50 or 65 \AA) and high specific surface area were obtained after the longer ageing times (**1TEc** and **1TEd**, Table 1, entries 14 and 15). Fig. 1 shows the N_2 adsorption–desorption isotherms of xerogels obtained from **1** with TBAF after ageing 6 days. A comparison between these four xerogels was of great interest. The xerogels **1TAa** (curve a) and **1TBa** (curve b) were prepared at -20°C and aged at -20°C and $+55^{\circ}\text{C}$ respectively (Table 1, entries 2 and 5), whereas **1TDa** (curve c) and **1TEb** (curve d) were gelled at $+55^{\circ}\text{C}$ and aged at -20°C and $+55^{\circ}\text{C}$ respectively (Table 1, entries 11 and 13). The xerogels **1TBa** and **1TEb** exhibited very similar textural properties (same specific surface area, same microporous volume, very close mesopore sizes—*cf.* Table 1, and same N_2 adsorption–desorption isotherms—*cf.* Fig. 1, curves b and c). This result could be indicative that the texture of the xerogels might be controlled during the ageing time, and that the temperature of ageing was an important parameter. Comparison between **1TAa** and **1TBa** illustrated this fact very well. In the same way, **1TAa** and **1TDa** (Table 1, entries 2 and 11) gelled respectively at -20°C and $+55^{\circ}\text{C}$ and aged at the temperature -20°C had also quite similar textural characteristics (lower specific surface area, micro and mesoporosity and no narrow pore size distribution).

When the catalyst was HCl, the xerogels **1HAa** and **1HAb** (Table 1, entries 16 and 17) obtained after 0 and 3 days of ageing exhibited no significant specific surface area. After 6 days, a highly microporous solid (80%) was obtained with a BET surface of $540\text{ m}^2\text{ g}^{-1}$. After longer ageing times, the specific surface area decreased, as well as the microporous volume (**1HAD**, **1HAe**, Table 1, entries 19 and 20).

In the case of the non-ionic nucleophilic catalyst DMAP, the ageing time had a high influence on the textural properties of the resulting xerogels. When no ageing was performed (**1DAa**, Table 1, entry 21), no specific surface area was observed. When the ageing time increased from 3 to 30 days, the specific surface area increased from 475 to $1160\text{ m}^2\text{ g}^{-1}$ whereas the microporous volume decreased from 65 to 15% (**1DAb** to **1DAe**,

†The level of condensation has been evaluated according to the following formula:²⁹

$$\text{level of condensation} = \frac{0.5(\text{area}T^1) + 1.0(\text{area}T^2) + 1.5(\text{area}T^3)}{1.5} \quad (1)$$

Table 1, entries 22–25). In each case no narrow pore size distribution was observed.

The length of ageing did not change drastically the densities of the gels. In the case of TBAF catalyst, they ranged between 1.42 and 1.46 g cm⁻³ at -20 °C and between 1.45 and 1.54 g cm⁻³ at +55 °C. They appeared in the same range with HCl catalyst (range 1.40–1.47 g cm⁻³) and slightly lower in the case of non-ionic nucleophile DMAP (1.37–1.44 g cm⁻³). This result is consistent with the previous results obtained with these catalysts.^{22,24}

All the solids obtained from **1** exhibited a moderate to high affinity for water. The weight increases in a 60% humidity atmosphere at 25 °C ($E_{0.6}$) have been determined. The higher reaction temperature (+55 °C) appeared to favor the gels having the lower affinity for water: range 20 to 34% at -20 °C or +20 °C and 17 to 21% at +55 °C with TBAF catalyst.

Xerogels obtained from **2**

²⁹Si CP MAS NMR data. The ²⁹Si CP MAS NMR data of the xerogels obtained from **2** are reported in Table 2. In the case of TBAF catalyst, when no ageing was performed (**2TAa**, Table 2, entry 1) very low percentages of T⁰ (δ -45.4 ppm) and T¹ (δ -51.0 ppm) units were observed whereas after 6, 15 and 30 days of ageing, only T² (δ -59.4 ppm) and T³ (δ -66.2 ppm) substructures were present. The xerogels **2TAa–2TAd** (Table 2, entries 1–4) were highly polycondensed (85–91%) whatever the ageing time. Using HCl as catalyst, the xerogels were moderately polycondensed (64–66%) in all cases and T¹, T² and T³ substructures were observed whatever the ageing time.

Texture, density and hydrophilic character of the solids. The specific surface areas of the xerogels obtained from **2** are reported in Table 2. They depended strongly on the catalyst as previously observed.²⁴ With HCl catalyst no significant specific surface area was observed. In the case of TBAF as catalyst, the specific surface area varied with the ageing time. When no ageing was performed (**2TAa**, Table 2, entry 1) no significant specific surface area was observed. Increasing the ageing time led to a small increase of the surface. The solids were mainly mesoporous and after 30 days of ageing mesopores of 45 Å (**2TAd**, Table 2, entry 4) were obtained.

The densities of xerogels obtained from **2** ranged between 1.12 and 1.18 g cm⁻³ and were not influenced by the ageing conditions. The solids were highly hydrophobic in all cases.

The results presented here show that the level of condensation at silicon atoms for xerogels mainly depended on the nature of the organic group and the catalyst, and was only weakly influenced by the ageing time. The lowest degrees of condensation were obtained using HCl as catalyst for both compounds **1** and **2**. The percentages of the Tⁱ site populations for long ageing times indicated the increase of polycondensation at silicon atoms in all cases as normally expected. A different behavior corresponding to changes in Tⁱ distribution with the same level of polycondensation at silicon atoms has been already reported in the case of NaOH catalyst:³⁶ it was explained by Si–O–Si bond cleavage due to nucleophilic attack of OH⁻ at silicon atoms which induces redistribution reactions. The specific surface areas and porosities of xerogels appeared highly dependent on the ageing conditions of the gels. After long ageing times, the solids obtained were mainly mesoporous and exhibited high specific surface areas, whereas with short ageing times, microporous solids or solids exhibiting no significant specific surface area were obtained.

Conclusion

The results presented here conclude our studies concerning the influence of the kinetic parameters on the hydrolysis polycondensation reactions involved in sol–gel process. They

confirm that hybrid materials obtained by hydrolytic polycondensation are under kinetic control and that the textural properties (specific surface area, porosity, ...) are controlled by the experimental parameters of the reaction.^{19–24} The level of condensation at silicon atoms for xerogels mainly depends on the nature of the organic group, the solvent, the catalyst, the temperature and the ageing conditions (length and temperature) have only a minor influence. In contrast, the ageing conditions, as well as the other parameters, were fundamental for the textural properties of the xerogels. The solids prepared at low temperature with short ageing times were mainly microporous and exhibited no narrow pore size distribution. Increasing the temperature either of the gelation and/or ageing, and increasing the length of ageing led to the formation of mesoporous solids having high specific surface areas and narrow pore size distribution.

The results presented here strengthen the importance of the kinetic control of the solid formation. The sum of all results,^{19–24,36} obtained during these studies, would suggest that the obtention of mesoporous hybrid organic–inorganic materials having high specific surface areas and a narrow pore size distribution is favoured whatever the organic group by high temperature and/or long ageing times of gelification. They confirm that the level of condensation at silicon atoms and the texture are not determined during the same steps of the process: the texture being matured during the last steps and particularly the ageing.

References

- 1 J. Rouxel, *Chem. Scr.*, 1988, **28**, 33; J. Livage, *Chem. Scr.*, 1988, **28**, 9.
- 2 S. Sakka and K. Kamiya, *J. Non-Cryst. Solids*, 1980, **42**, 403.
- 3 C. J. Brinker and G. W. Scherer, *Sol–Gel Science: The Physics and Chemistry of Sol–Gel Processing*, Academic Press, San Diego, 1990.
- 4 L. L. Hench and J. K. West, *Chem. Rev.*, 1990, **90**, 33.
- 5 C. D. Chandler, C. Roger and M. J. Hampden-Smith, *Chem. Rev.*, 1993, **93**, 1205.
- 6 J. Livage, M. Henry and C. Sanchez, *Prog. Solid State Chem.*, 1988, **18**, 259.
- 7 R. J. P. Corriu and D. Leclercq, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1420.
- 8 D. A. Loy and K. J. Shea, *Chem. Rev.*, 1995, **95**, 1431 and references therein.
- 9 S. T. Hobson and K. J. Shea, *Chem. Mater.*, 1997, **9**, 616.
- 10 P. Judeinstein and C. Sanchez, *J. Mater. Chem.*, 1996, **6**, 511.
- 11 B. Lebeau, S. Brasselet, J. Zyss and C. Sanchez, *Chem. Mater.*, 1997, **9**, 1012.
- 12 U. Schübert, N. Hüsing and A. Lorenz, *Chem. Mater.*, 1995, **7**, 2010.
- 13 R. J. P. Corriu, *Polyhedron*, 1998, **17**, 925.
- 14 G. Cerveau and R. J. P. Corriu, *Coord. Chem. Rev.*, 1998, **180** (part 2), 1051 and references therein.
- 15 R. J. P. Corriu, *Angew. Chem., Int. Ed.*, 2000, **39**, 1376.
- 16 S. W. Carr, M. Motevalli, D. Li Ou and A. C. Sullivan, *J. Mater. Chem.*, 1997, **7**, 865.
- 17 F. Ribot and C. Sanchez, *Comments Inorg. Chem.*, 1999, **20**, 327 and references therein.
- 18 Special Issue, *New J. Chem.*, 1994, **18**
- 19 G. Cerveau, R. J. P. Corriu and C. Fischmeister-Lepeyre, *J. Mater. Chem.*, 1999, **9**, 1149.
- 20 G. Cerveau, R. J. P. Corriu and C. Lepeyre, *J. Organomet. Chem.*, 1997, **548**, 99.
- 21 G. Cerveau, R. J. P. Corriu, C. Lepeyre and P. H. Mutin, *J. Mater. Chem.*, 1998, **8**, 2707.
- 22 G. Cerveau, R. J. P. Corriu and E. Framery, *Polyhedron*, 2000, **19**, 307.
- 23 G. Cerveau, R. J. P. Corriu and E. Framery, *Chem. Commun.*, 1999, 2080.
- 24 G. Cerveau, R. J. P. Corriu and E. Framery, *J. Mater. Chem.*, 2000, **10**, 1617.
- 25 D. F. Schriver, *The manipulation of air-sensitive compounds*, MacGraw-Hill, New York, 1969.
- 26 R. J. P. Corriu, J. Moreau, P. Thépot and M. Wong Chi Man, *Chem. Mater.*, 1992, **4**, 1217.

- 27 H. W. Oviatt Jr., K. J. Shea and J. H. Small, *Chem. Mater.*, 1993, **5**, 943.
- 28 D. A. Skoog, D. M. West and F. J. Holler, *Fundamentals of analytical chemistry*, Sanders College Publishing, International Edition, 1992, p. 873.
- 29 K. J. Shea, D. A. Loy and O. Webster, *J. Am. Chem. Soc.*, 1992, **114**, 6700.
- 30 S. J. Gregg and S. W. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, London, 1982.
- 31 S. Brunauer, P. H. Emmet and E. Teller, *J. Am. Chem. Soc.*, 1938, **60**, 309.
- 32 S. Brunauer, L. S. Deming, W. S. Deming and E. Teller, *J. Am. Chem. Soc.*, 1940, **62**, 1723.
- 33 E. Baret, L. Joyner and P. Halenda, *J. Am. Chem. Soc.*, 1951, **73**, 373.
- 34 K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquérol and T. Siemieniowska, *Pure Appl. Chem.*, 1985, **57**, 603.
- 35 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.
- 36 G. Cerveau, R. J. P. Corriu and E. Framery, *C. R. Acad. Sci.*, in the press.