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Influence of kinetic parameters on the textural and chemical properties of silsesquioxane materials obtained by sol–gel process

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The hydrolytic sol–gel polymerization of a 'rigid' molecular precursor 1,4-C_6H_4 $[Si(OMe)_3]_2$ **1** and a more 'flexible' one 1,4-$C_6H_4[CH_2CH_2Si(OMe)_3]_2$ **2** was investigated varying the experimental conditions. Two solvents, MeOH and THF, were employed. The influence of the catalyst has been determined by using TBAF (tetrabutylammonium fluoride) or NH_4F as nucleophilic catalysts, NH_4OH and NaOH as basic catalysts and HCl as acid catalyst. The effect of concentration of the precursor was also studied. Molecular precursor **1** led always to hydrophilic solids with similar degrees of condensation (63–67%). In all cases high specific surface areas and poor chemical reactivity towards $Cr(CO)_6$ were observed and the solvent had an influence on the porosity. By contrast, the precursor **2** led to hydrophobic solids and the texture, the degree of condensation and the reactivity with $Cr(CO)_6$ were strongly dependent on the solvent, the catalyst and the concentration. In MeOH no significant specific surface areas were observed, whereas in THF a high specific surface area was observed with TBAF catalysis at both precursor concentrations studied. Degrees of condensation were higher in THF. All the kinetic parameters involved in the hydrolytic sol–gel polymerization of molecular organosilicon precursors were of importance on the properties of the resulting solids, the main factor being the geometry of the organic unit.

Introduction

The sol–gel process offers an access to a wide variety of materials under very mild conditions.[1–7] We have focused our interest on the study of organic–inorganic hybrid materials obtained by hydrolysis–polycondensation of organically substituted alkoxysilanes. In such materials both organic and inorganic units are bound *via* at least two stable Si–C bonds. A large variety of organic units have been incorporated in inorganic matrices and it has been shown that changing the nature of the organic groups induces drastic changes in the macroscopic properties of the hybrid solid such as specific surface area, porosity and hydrophilicity.[8–17]

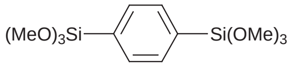
In a previous work,[18] we have shown that the structure of the organic precursor is a determining parameter for the solid state properties of xerogels containing aromatic groups. Moreover the influence of the organic precursor on both the physical and chemical properties of the hybrid solids has been evidenced with gels formed very precisely under the same experimental conditions.[18] In a preliminary report, we have pointed out the drastic influence of the geometry of the 'rigid' or 'flexible' organic group on the solid organization.[18] Molecular precursors containing a 'rigid' organic group lead to hydrophilic solids in which the organic groups are not accessible to chemical reagents and not detected by TOF-SIMS analysis.[19] By contrast, when the precusor contains a 'flexible' organic moiety the solids obtained are hydrophobic and the organic groups are located at the surface reacting readily with $Cr(CO)_6$.[19]

The texture of the resulting solids is also highly dependent on the nature of the precursor. Precursors containing a 'rigid' organic group always lead to solids with high specific surface areas whatever the solvent. By contrast, when the precursor contains a 'flexible' organic spacer the texture of the resulting solids strongly depends on the solvent: solids prepared in MeOH have no significant specific surface area whereas in THF high specific surface areas are observed. These results and others obtained with different hybrid materials suggest a possible kinetic control of the texture.

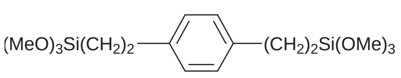
In this context, we decided to investigate the influence of other kinetic parameters involved in the hydrolysis polycondensation reactions. We report here, results concerning the influence of the catalyst, the concentration of the precursor and the solvent on the chemical and textural properties of xerogels obtained from two precursors having different geometries, a 'rigid' one and a 'flexible' one.

Results

The sol–gel polymerization of the molecular precursors **1** having a 'rigid' spacer and **2** containing a more 'flexible' organic group have been investigated. The influence of the solvent, the catalyst and the concentration of precursor on the chemical and textural properties of the resulting solids has been studied. The solvents employed were MeOH and THF. Three types of catalysts were used: nucleophilic, basic and acidic. Two concentrations of precursor were investigated. In each case the xerogels were characterized by NMR spectroscopy, the texture was determined and the chemical reactivity towards complexation reaction with $Cr(CO)_6$ was studied.



1

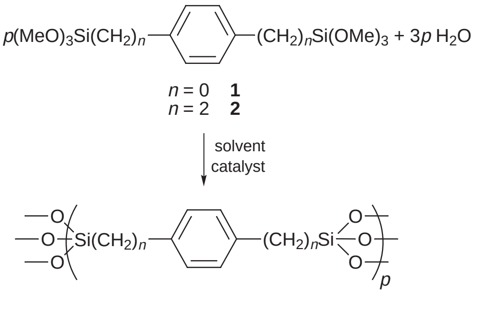


2

Influence of the catalyst and the solvent

(a) Sol–gel processing of 1. Five different catalysts have been used : nucleophiles NH_4F and TBAF, bases NaOH and NH_4OH and acid HCl. The amount of catalyst was 1 mol% and the concentration of **1** was 0.5 mol l^{-1} in all cases. A stoichiometric amount of water was used. Two sets of reactions were performed, in MeOH and in THF [reaction (1)].

When the reaction was performed in MeOH, opaque gels were obtained whereas in THF transparent gels formed in all



(1)

cases within various periods of time.The gels were allowed to age for five days and were then powdered, washed with ethanol, acetone and diethyl ether. The powders were dried *in vacuo* at 120 °C for 3 h.

(b) Characterization and spectroscopic data of xerogels obtained from 1. *NMR data.* These xerogels were studied by ^{13}C and ^{29}Si CP MAS NMR spectroscopies. The ^{13}C CP MAS NMR spectra of xerogels showed that the organic fragment was not modified. They displayed a resonance at δ 133.7 assigned to aromatic carbons and another at δ 50.4 attributed to residual methoxy groups in all cases. However the intensity of this signal at δ 50.4 was very weak when THF was employed, indicative of a higher degree of hydrolysis in THF than in MeOH, in good agreement with the elemental analyses reported in the experimental section.

^{29}Si CP MAS NMR clearly established that the Si–C bond was retained within the gel in all cases.[20] The absence of any Q signal corresponding to $SiO_{4/2}$ units[21] in the range δ -100 to -110 indicated that the integrity of the organic moiety has been maintained during the hydrolysis–polycondensation process. The ^{29}Si CP MAS NMR spectra displayed in all cases three resonances assigned to substructures T^1 [C–Si(OR)$_2$ OSi, $\delta \approx -61$], T^2 [C–Si(OR)(OSi)$_2$ $\delta \approx -68$] and T^3 [C–Si(OSi)$_3$, $\delta \approx -78$]. The ^{29}Si CP MAS NMR characteristics were very similar when the xerogels were prepared in MeOH and in THF. Although quantitative conclusions are not valid for CP MAS NMR spectra, deconvolution of the ^{29}Si resonances and integration of the areas allowed an estimation of the degree of condensation in the network. Indeed previous work [9,18] has shown that single pulse experiments did not reveal any significant variation in relative peak intensity from the CP MAS spectra without hydrogen atoms in the direct vicinity of the studied nucleus. All the samples had similar degrees of condensation (Table 1) lying in the range of 63–67%, whatever the catalyst and the solvent. Thus, whatever the catalyst and solvent, the condensation was always incomplete. This result was in agreement with the elemental analysis which showed that the hybrid gels deviated from the ideal stoichiometry based on totally polycondensed silsesquioxane materials (see Experimental section). These analyses revealed an excess of carbon and hydrogen indicating the presence of residual hydroxy and methoxy groups.

Hydrophilicity. All the solids obtained from **1** exhibited significant hydrophilic character independent of the gelation solvent and the catalyst. Weight increases in a 60% humidity atmosphere at 25 °C ($E_{0.6}$) are reported in Table 1.

BET measurements. The specific surface areas of the xerogels were determined by nitrogen adsorption experiments at 77 K using the BET method. Values were very high (between 370 and 773 $m^2 g^{-1}$) depending on the solvent and the catalyst (Table 1). They were higher when the reaction was performed in MeOH whatever the catalyst. Use of an acid catalyst led to higher specific surface areas in both solvents. The texture of the solids has been studied using adsorption–desorption isotherms. The shape of the curves was similar, characteristic of microporous solids, however when MeOH was used, a weak hysteresis loop was observed, indicating a low mesoporous contribution.[22]

Adsorption–desorption isotherms of **1ME** and **1TE** are shown in Fig. 1. The determination of the porous volume by the BJH method[23] and the evaluation of the microporous volume by the analysis of the t-plot diagram have been performed in each case. The BET specific surface areas and porous volumes of the xerogels are reported in Table 2. The microporous volume represented 50–60% of the total porous volume when the hydrolysis was performed in MeOH, and it

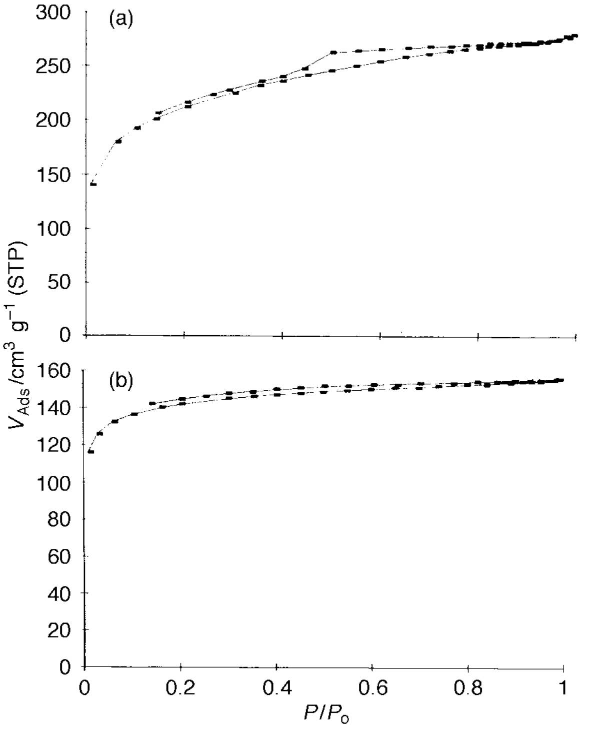


Fig. 1 N_2 adsorption–desorption isotherms of (a) xerogel **1ME** and (b) **1TE**.

Table 1 Characterization of the xerogels obtained by hydrolysis and polycondensation of **1** (0.5 mol l^{-1}) at room temperature

Solvent	Catalyst	Xerogel	Degree of condensation (%)	$S_{BET}/m^2 g^{-1}$	$E_{0.6}$ (%)	Degree of complexation (%)
MeOH	TBAF	**1MA**	64	549	21–23	18
MeOH	NH_4F	**1MB**	63	558	20–22	22
MeOH	NH_4OH	**1MC**	63	705	24–28	20
MeOH	NaOH	**1MD**	64	628	18–22	36
MeOH	HCl	**1ME**	64	773	26–28	24
THF	TBAF	**1TA**	67	370	18–22	11
THF	NH_4F	**1TB**	65	388	21–22	25
THF	NH_4OH	**1TC**	67	384	19–20	8
THF	NaOH	**1TD**	64	528	24	8
THF	HCl	**1TE**	65	538	25–26	16

Table 2 N_2 adsorption–desorption data of xerogels obtained from **1**

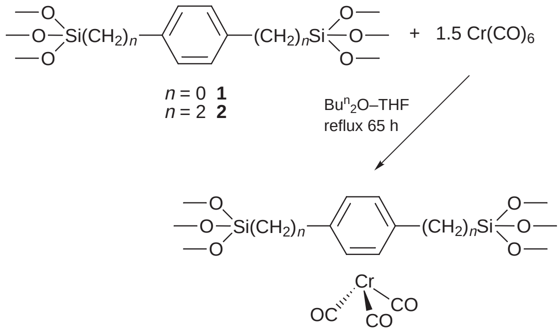
Xerogel	S_{BET}/ $m^2\ g^{-1}$	$V_{Tot}{}^a$/ $cm^3\ g^{-1}$	$V_{Ads}{}^b$/ $cm^3\ g^{-1}$	$V_{Des}{}^b$/ $cm^3\ g^{-1}$	$V_{Micro}{}^c$/ $cm^3\ g^{-1}$	c
1MA	549	0.27	0.11	0.11	0.16	470
1MB	558	0.34	0.20	0.20	0.14	—
1MC	705	0.38	0.20	0.20	0.20	425
1MD	628	0.32	0.14	0.14	0.18	474
1ME	773	0.43	0.23	0.23	0.21	317
1TA	370	0.19	0.04	0.03	0.15	814
1TB	388	0.16	0.03	0.01	0.13	—
1TC	384	0.17	0.03	0.01	0.14	652
1TD	528	0.24	0.06	0.04	0.18	1216
1TE	538	0.24	0.05	0.04	0.19	2300

[a] $P/P_0 = 0.99$. [b] Cumulative pore volume of pores between 17 and 3000 Å diameter. [c] Estimated by the t-plot method, using Harkins and Jura standard isotherm and thickness range between 4 and 6 Å.[25]

was higher in the case of THF, since it ranged between 75 and 82%. The BET constant c was very high in all cases which is also indicative of microporosity.

(c) Chemical reactivity of xerogels obtained from 1. The accessibility of the aromatic groups of the hybrid network, using the complexation reaction of aryl fragments with $Cr(CO)_6$, has been used as a tool for studying the solid arrangement.[13a]

The silsesquioxane materials obtained from **1** were treated with $Cr(CO)_6$ under heterogeneous conditions in a mixture of $Bu^n{}_2O$–THF (20:80) at 118 °C [Reaction (2)]. The complexation reaction was evidenced by FTIR and ^{13}C CP MAS NMR spectroscopies as described previously.[18] FTIR spectra showed new absorption bonds at *ca.* 1970 and 1880 cm^{-1} due to carbonyl groups, the intensity of which depended on the degree of complexation with $Cr(CO)_6$. The ^{13}C CP MAS NMR spectra clearly showed the presence of a mixture of uncomplexed aryl and aryl–$Cr(CO)_3$ units: spectra showed signals corresponding to carbonyl groups at $\delta \approx 234$, uncomplexed aromatics at $\delta \approx 134$ and aryl–Cr $(CO)_3$ at $\delta \approx 94$. When the degree of complexation was very low, the reaction with $Cr(CO)_6$ was evidenced by FTIR spectroscopy, the CO ligands and complexed aromatics not being detected by ^{13}C CP MAS NMR. The degree of complexation was determined by EDS and chemical analysis. The results deduced from elemental analysis are reported in Table 1. Despite their high specific surface areas, the xerogels led to poor degrees of complexation (8–36%) whatever the solvent and the catalyst. This suggests an organization of the solid in which only a few aromatic groups are accessible to $Cr(CO)_6$. These results are in agreement with TOF-SIMS analysis of the surface of xerogels obtained from **1**, only ions $SiOH^+$ at m/z 45 are detected, in accord with hydrophilicity and poor chemical reactivity.[19]



(2)

(d) Sol–gel processing of 2. The organic precursor **2** was hydrolysed under the same conditions as **1**. When the reaction was performed in MeOH, white precipitates were obtained with TBAF and NaOH catalyst, a resin with NH_4OH while transparent gels formed with NH_4F and HCl catalysts. When the solvent was THF, transparent gels were obtained in all cases, as expected when a basic NH_4OH catalyst was used. In this case no reaction occurred after several months . The same processing (ageing, washing and drying) was used and, the xerogels were isolated as white powders.

(e) Characterization and spectroscopic data of xerogels obtained from 2. *NMR data.* The solid state NMR spectroscopic studies of the xerogels obtained from **2** clearly showed that the Si–C bond was not cleaved during the hydrolysis–polycondensation process. ^{13}C CP MAS NMR spectra exhibited resonances at δ 127.5 and 144 assigned to aromatic carbons, others at δ 14 and 29 attributed to CH_2 carbons and another at δ 50 due to residual methoxy groups in all cases. Similarly as for xerogels obtained from **1**, when THF was used, the intensity of the signal at δ 50 was very weak, due to a higher degree of hydrolysis in THF. ^{29}Si CP MAS NMR spectra of xerogels obtained in MeOH displayed the four resonances assigned to T^0 (δ −42), T^1 (δ −50), T^2 (δ −59) and T^3 (δ −67) substructures when TBAF (**2MA**), NH_4OH (**2MC**) and NaOH (**2MD**) were used as catalyst. When NH_4F (**2MB**) or HCl (**2ME**) were used only T^1, T^2 and T^3 substructures were observed. It is interesting that for **2MB** and **2ME** monolithic gels were obtained. However the degree of condensation was estimated and found to be in the same range (59–63%) whatever the catalyst (Table 3).

With THF as solvent, the xerogels appeared more polycondensed than in MeOH. No resonance at δ —42 assigned to T^0 substructure was detected. The degrees of condensation estimated from deconvoluted T peaks were higher being in the range 73–87% (Table 3). This was particularly pronounced for **2TA** and **2TD** where the T^3 substructures were more intense. These results are in accord with elemental analyses as observed for **1** (see Experimental section) and IR spectra which exhibited a weak (νOH) vibration at *ca.* 3630 cm^{-1}.

Hydrophilicity. The hydrophilic character of all the xerogels obtained from **2** was very low (Table 3).

BET measurements. The nitrogen BET measurements gave no significant specific surface area in all cases ($<10\ m^2\ g^{-1}$), except for **2TA** which exhibited a high surface area ($565\ m^2\ g^{-1}$).

The adsorption–desorption isotherm of **2TA** was characteristic of a solid exhibiting micro- and meso-porosity (Fig. 2). The microporous volume was estimated to be *ca.* 20% from the analysis of the t-plot diagram.

(f) Chemical reactivity of xerogels obtained from 2. In the same way as for xerogels obtained from **1**, the silsesquioxane materials obtained from **2** were treated with $Cr(CO)_6$ under the same experimental conditions (reaction 2) .The complexation reaction was monitored by FTIR and ^{13}C CP MAS NMR spectroscopies and the degree of complexation was deduced from elemental analysis (Table 3). In all cases the reactivity was high (42–92%). However higher degrees of complexation were obtained when the xerogels were prepared in MeOH. For example, **2ME** was almost quantitatively complexed by $Cr(CO)_3$ (92%).

The decrease of reactivity for gels prepared in THF might be attributed to the higher degree of condensation at silicon of the hybrid solids which induces a lower swelling of the solid corresponding to a lower accessibility of the organic groups.

The xerogel **2MB** exhibited a rather low reactivity (42%), although its spectroscopic and textural characteristics were similar to those of the highly reactive solid **2ME** (92%). Scanning electron microscopy (SEM) was the only method which allowed to establish a difference between **2MB** and

Table 3 Characterization of the xerogels obtained by hydrolysis and polycondensation of **2** (0.5 mol l^{-1}) at room temperature

Solvent	Catalyst	Xerogel	Degree of condensation (%)	S_{BET}/m^2 g^{-1}	$E_{0.6}$ (%)	Degree of complexation (%)
MeOH	TBAF	**2MA**	62	<10	2	84
MeOH	NH_4F	**2MB**	63	<10	3	42
MeOH	NH_4OH	**2MC**	62	<10	3	76
MeOH	NaOH	**2MD**	59	<10	2	62
MeOH	HCl	**2ME**	61	<10	2	92
THF	TBAF	**2TA**	87	565	5–6	64
THF	NH_4F	**2TB**	73	<10	3	72
THF	NH_4OH	no gel	—	—	—	—
THF	NaOH	**2TD**	83	<10	2	63
THF	HCl	**2TE**	73	<10	4	53

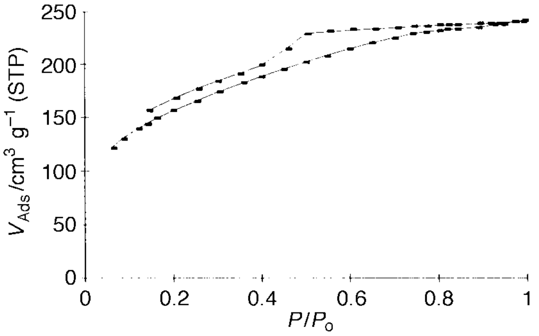


Fig. 2 N_2 adsorption–desorption isotherm of xerogel **2TA**.

2ME:**2ME** exhibited an irregular granularity as for other xerogels whereas **2MB** consisted of monodispersed spherical particles (Fig. 3).

Influence of the concentration

The organic precursors **1** and **2** have also been hydrolysed as 1 mol l^{-1} solutions in MeOH and in THF using TBAF catalyst (1 mol%) at room temperature.

1 gave an opaque gel in MeOH whereas a transparent gel formed in THF. A white precipitate was obtained in MeOH and a transparent gel in THF starting from **2**. Reaction times were shorter when using higher concentrations. After usual treatment, the xerogels were characterized and data are reported in Table 4.

The ^{29}Si and ^{13}C CP MAS NMR spectra of xerogels obtained from **1** and **2** at 1 mol l^{-1} concentration were similar, with no changes in the degree of condensation being observed. However drastic changes in the textural properties of the solid obtained from **1** were observed. The solids **1MAM** and **1TAM** exhibited very high specificic surface areas, 1062 and 1256 m^2 g^{-1} respectively, two or three times higher than at a 0.5 mol l^{-1} concentration. Nitrogen adsorption–desorption experiments led to totally different isotherms. **1MAM** presented a type IV isotherm[22] characteristic of a mesoporous solid, without narrow pore size distribution. For **1TAM**, the isotherm corresponded to a mesoporous solid with a low microporous contribution estimated at *ca.* 20% (Fig. 4).

The hydrophilic character and the degrees of complexation with $Cr(CO)_6$ were similar for the two concentrations studied.

In the case of **2,** the concentration of the precursor had no influence on the textural properties of solids **2MAM** and **2TAM** and BET surface areas were similar to those of **2MA** and **2TA**. The solid **2TAM** was mainly mesoporous with *ca.* 25% of micropores. By contrast, a drastic difference appeared in the chemical reactivity of solids **2MAM** and **2TAM** which led to low degrees of complexation with $Cr(CO)_6$, 26 and 38%, respectively compared to **2MA** and **2TA** which gave 84 and 64% respectively. Since the degrees of condensation around silicon were in the same range, this decrease of the reactivity might be attributed to a different structure of the solids hindering the accessibility of the aromatic groups.

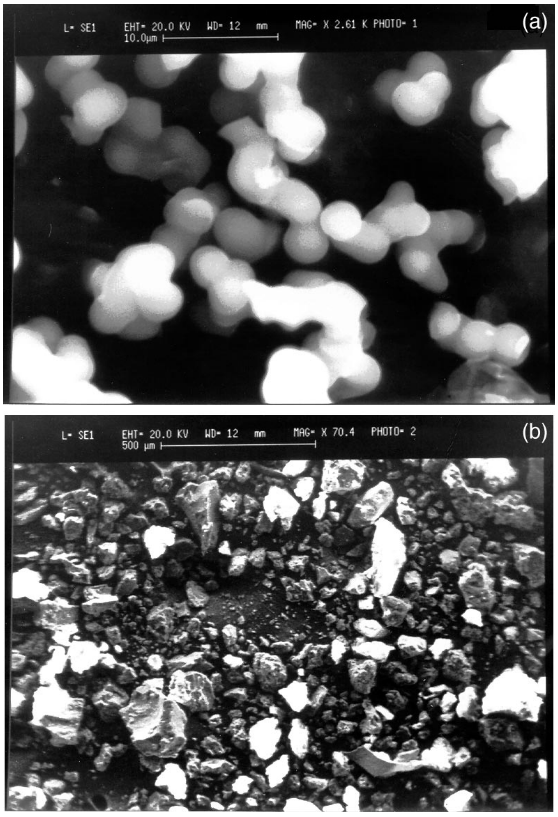


Fig. 3 SEM image of (a) **2MB** and (b) **2ME**.

Discussion

The results presented here show that both physical and chemical properties of silsesquioxane materials obtained by hydrolysis–polycondensation reactions are drastically dependent on all the experimental parameters which have been studied. These parameters: nature of the catalyst, nature of the solvent, nature and concentration of the substrate are involved in the kinetic law of the polycondensation process. However, it is possible to establish that the essential parameter is the nature of the organic group *i.e.* 'rigid' or 'flexible' as shown in Fig. 5(a) and (b).

The molecular precursor containing a 'rigid' organic group led always to hydrophilic solids with similar degrees of condensation whatever the catalyst, the solvent and the concentration. In all cases, these solids had high specific surface areas and absence of a narrow pore size distribution. When THF was employed the surface area was lower than with MeOH and the solids were mainly microporous (*ca.* 80%). Increasing the concentration, led to an increase of the specific surface area

Table 4 Characterization of the xerogels obtained by hydrolysis–polycondensation of **1** and **2** (1 mol l^{-1}) at room temperature in the presence of 1 mol% TBAF

Solvent	Xerogel	Degree of condensation (%)	S_{BET}/m^2 g^{-1}	$E_{0.6}$ (%)	Degree of complexation (%)
MeOH	**1MAM**	66	1062	19–23	22
THF	**1TAM**	65	1256	26	12
MeOH	**2MAM**	63	<10	3	26
THF	**2TAM**	85	531	4–7	38

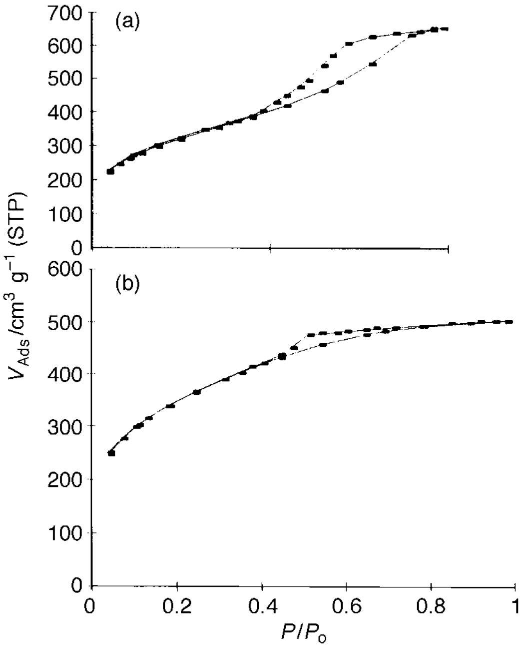


Fig. 4 N_2 adsorption–desorption isotherms of (a) xerogel **1MAM** and (b) **1TAM**.

in all cases and induced changes in the porosity of the solids: at 0.5 mol l^{-1} concentration in MeOH, the xerogel was micro- and meso-porous whereas at 1 mol l^{-1} concentration it was mesoporous with absence of a narrow pore size distribution. When THF was used, it was mainly microporous (*ca.* 80%) at 0.5 mol l^{-1} but only *ca.* 20% at 1 mol l^{-1}. Poor reactivity towards $Cr(CO)_6$ was observed.

By contrast, when the precursor contained a 'flexible' organic moiety, the texture, the degree of condensation and the reactivity of the resulting xerogels strongly depended on the solvent, the catalyst and the concentration. The solids were hydrophobic in all cases. The xerogels prepared in methanol had no significant specific surface area, whereas in THF a high specific surface area was observed when the catalyst was TBAF at both concentrations. The two solids were mesoporous with *ca.* 20% of micropores. The degrees of condensation depended on the solvent and were higher in THF. The degree of complexation with $Cr(CO)_6$ was high in all cases and decreased with increased concentration of precursor.

Conclusion

The results presented here illustrate the tenuous link between the macroscopic data which describe the texture of the solids and the microscopic parameters which control the kinetics of all the chemical reactions involved in the hydrolysis–poycondensation process: nature of the solvent, nature of the catalyst, nature and concentration of the substrate and geometric features of the organic group.

The main conclusion is that the solids obtained by the sol–gel process are better described as kinetically controlled solids instead of thermodynamically unstable materials.[1] Their instability corresponds to a kinetic evolution.

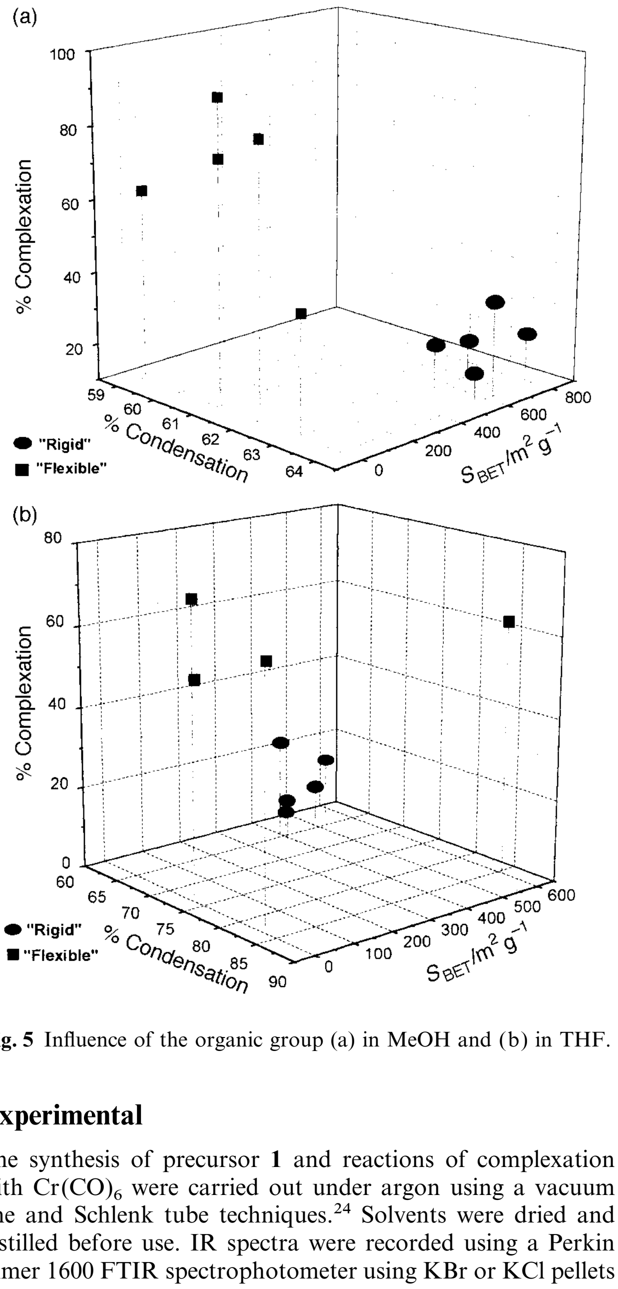


Fig. 5 Influence of the organic group (a) in MeOH and (b) in THF.

Experimental

The synthesis of precursor **1** and reactions of complexation with $Cr(CO)_6$ were carried out under argon using a vacuum line and Schlenk tube techniques.[24] Solvents were dried and distilled before use. IR spectra were recorded using a Perkin Elmer 1600 FTIR spectrophotometer using KBr or KCl pellets or by the DRIFT method. Solid state NMR spectra were obtained with a Bruker FTAM 300 spectrometer: ^{13}C CP MAS NMR at 75.47 MHz, recycling delay 5 s, contact time 5 ms; ^{29} Si NMR CP MAS NMR at 59.62 MHz, recycling delay 10 s, and contact time 2 ms. The spinning rate was 5000 Hz in both 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. Elemental analyses were carried out by the 'Service Central de Micro-Analyse du CNRS'. Oxygen percentages were deduced by difference. Scanning electron microscopy (SEM) analyses were performed using a Leica 5360 type Cambridge apparatus.

Compound **1** was prepared according to literature procedures[11a,13b] **2** was supplied commercially and purified before use.

Sol–gel processing

The preparation of xerogels was carried out according to the procedure already reported.[18] The specific surface areas and hydrophilic character of xerogels obtained from **1** are reported in Table 1, and from **2** in Table 3.

Xerogels obtained from 1

1MA and **1TA** have already been reported.[18]

Elemental analyses: calc. for $C_6H_4Si_2O_3$: C, 39.97; H, 2.23; Si, 31.15; O, 26.62%. Found for: **1MB** (gelation time, 60 min): C, 35.75; H, 3.46; Si, 23.70; O, 37.09% ($C_{7.08}H_{8.22}Si_2O_{5.48}$); **1MC** (gelation time, 150 min): C, 35.00; H, 4.30; Si, 25.50; O, 35.20% ($C_{6.26}H_{9.46}Si_2O_{4.88}$); **1MD** (gelation time, 165 min): C, 37.95; H, 3.94; Si, 24.60; O, 33.51% ($C_{7.26}H_{8.96}Si_2O_{4.82}$); **1ME** (gelation time, 95 min): C, 39.11; H, 3.77; Si, 26.70; O, 30.42% ($C_{6.84}H_{7.86}Si_2O_{4.00}$); **1TB** (gelation time, 10 min): no analyses obtained; **1TC** (gelation time, 95 min): C, 33.75; H, 3.63; Si, 28.40; O, 34.22% ($C_{5.56}H_{7.12}Si_2O_{4.23}$); **1TD** (gelation time, 130 min): C, 35.51; H, 3.21; Si, 27.25; O, 34.03% ($C_{6.08}H_{6.54}Si_2O_{4.36}$); **1TE** (gelation time, 85 min): C, 35.74; H, 3.12; Si, 26.20; O, 34.95% ($C_{6.38}H_{6.64}Si_2O_{4.68}$); **1MAM** (gelation time, 4 min): C, 39.85; H, 3.68, Si, 25.30; O, 31.17% ($C_{7.34}H_{8.10}Si_2O_{4.30}$); **1TAM** (gelation time, 4 min): C, 39.97; H, 2.23; Si. 31.15; O, 26.62% ($C_{7.08}H_{7.80}$ $Si_2O_{4.26}$).

Xerogels obtained from 2

2MA and **2TA** have been reported previously.[18]

Elemental analyses: calc. for $C_{10}H_{12}Si_2O_3$: C, 50.81; H, 5.11; Si, 23.76; O, 20.30%. Found for: **2MB** (gelation time, 40 min): C, 50.16; H, 6.34; Si, 17.14; O, 26.36% ($C_{13.66}H_{20.62}Si_2O_{5.36}$); **2MC** (resin obtained after 2 months): C, 49.86; H, 6.35; Si, 17.90; O, 25.89% ($C_{13.08}H_{20.56}Si_2O_{4.98}$); **2MD (**precipitate after 90 min): C, 49.13; H, 6.37; Si, 20.10; O, 24.40% ($C_{11.52}H_{17.80}Si_2O_{4.28}$); **2ME** (gelation time, 270 min): C, 49.70; H, 6.25; Si, 19.50; O, 24.55% ($C_{11.96}H_{17.96}Si_2O_{4.42}$); **2TB** (gelation time, 65 h); C, 49.99; H, 5.70; Si, 22.32; O, 21.99% ($C_{10.53}H_{13.36}Si_2O_{3.46}$); **2TD** (gelation time, 6 h): C, 49.71; H, 5.57; Si, 23.00; O, 21.72% ($C_{10.06}H_{13.47}Si_2O_{3.31}$); **2TE** (gelation time; 30 min): C, 49.79; H, 5.73; Si, 20.30; O, 24.18% ($C_{11.47}H_{15.73}Si_2O_{4.25}$); **2MAM** (precipitate after 10 min): C, 50.03; H, 6.30; Si, 20.30; O, 23.57% ($C_{11.54}H_{17.36}Si_2O_4$); **2TAM** (gelation time, 2 min): C, 49.36; H, 5.34; Si, 21.80; O, 23.50% ($C_{10.66}H_{13.74}Si_2O_{5.80}$).

Complexation reactions with $Cr(CO)_6$

Complexation reactions of the xerogels were carried out following the procedure reported earlier.[13a,18]

The pale green resulting solids were analysed by FTIR and NMR spectrocopies. The degrees of complexation were determined by chemical elemental analysis. The experimental ratio $(Cr/Si)_{exp}$ was determined from the elemental analysis and compared to the theoretical value $(Cr/Si)_{th}$ assuming a degree of complexation of 100%. The results obtained were confirmed by elemental EDS analysis.

Elemental analysis found for complexation from **1MB**: C, 36.51; H, 4.17; Cr, 3.70; Si, 20.10; O, 35.17% (Cr/Si = 0.11); **1MC**: C, 36.70; H, 4.05; Cr, 4.50; Si, 22.80; O, 31.95% (Cr/Si = 0.10); **1MD**: C, 36.13; H, 4.03; Cr, 7.15; Si, 20.60; O, 32.09% (Cr/Si = 0.18); **1ME**: C, 37.91; H, 4.12; Cr, 3.60; Si, 16.35; O, 38.02% (Cr/Si = 0.12); **1TB**: C, 35.45; H, 4.10; Cr, 4.55; Si, 20.00; O, 35.90% (Cr/Si = 0.125); **1TC**: C, 31.92; H, 3.92; Cr, 1.70; Si, 23.80; O, 38.66% (Cr/Si = 0.04); **1TD**: C, 35.46; H, 4.28; Cr; 1.65; Si, 22.45; O, 36.16% (Cr/Si = 0.04): **1TE**: C, 34.64; H, 3.93; Cr, 3.20; Si, 21.45; O, 38.02% (Cr/Si = 0.08); **1MAM**: C, 38.94; H,4.01; Cr, 4.80; Si; 22.40; O, 29.85% (Cr/Si = 0.11); **1TAM**: C, 39.09; H, 3.92; Cr, 2.75; Si, 24.75; O, 29.49% (Cr/Si = 0.06); **2MB**: C, 44.40; H, 5.49; Cr, 6.65; Si, 16.8; O, 26.66% (Cr/Si: 0.21); **2MC**: C, 44.31; H, 4.66; Cr, 9.85; Si, 13.80; O, 27.38% (Cr/Si = 0.38); **2MD**: C, 43.15; H, 5.09; Cr, 9.05; Si, 15.45; O, 27.46% (Cr/Si = 0.31); **2ME**: C, 41.24; H, 4.51; Cr, 12.25; Si, 14.00; O, 28.00% (Cr/Si = 0.46); **2TB**: C, 42.22; H, 4.57; Cr, 10.25; Si, 15.10; O, 27.86% (Cr/Si: 0.36); **2TD**: C, 42.60; H, 4.45; Cr, 9.70; Si, 16.45; O, 26.80% (Cr/Si = 0.315); **2TE**: C, 42.55; H, 4.63; Cr, 8.75; Si, 17.70; O, 26.37% (Cr/Si = 0.265); **2MAM**: C, 44.78; H, 5.59; Cr, 3.40; Si, 14.30; O, 31.93% (Cr/Si = 0.13); **2TAM**: C, 45.32, H, 4.91; Cr, 6.50; Si, 18.40; O, 24.87% (Cr/Si = 0.19).

References

1 C. J. Brinker and G. W. Scherer, *Sol–Gel Science: The Physics and Chemistry of Sol–Gel Processing*, Academic Press, San Diego, 1990.

2 L. L. Hench and J. K. West, *Chem. Rev.*, 1990, **90,** 33 and references therein.

3 D. A. Loy and K. J. Shea, *Chem. Rev.*, 1995, **95**, 1431 and references therein.

4 U. Schubert, N. Hüsing and A. Lorentz, *Chem. Mater.*, 1995, **7**, 2010 and references therein.

5 P. Judenstein and C. Sanchez, *J. Mater. Chem.*, 1996, **6,** 511.

6 R. J. P. Corriu and D. Leclercq, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1420 and references therein.

7 R. J. P. Corriu, *Polyhedron*, 1998, **17**, 925 and references therein.

8 K. J. Shea, D. A. Loy and O. W. Webster, *Chem. Mater.*, 1989, **1**, 574; K. J. Shea, D. A. Loy and O. Webster, *J. Am. Chem. Soc.*, 1992, **114**, 6700 and references therein; K. M. Choi and K. J. Shea, *J. Am. Chem. Soc.*, 1994, **116**, 9052; K. M. Choi and K. J. Shea, *Phys. Chem.*, 1994, **98**, 3207; K. M. Choi, J. C. Hemminger and K. J. Shea, *Phys. Chem.*, 1995, **99**, 4720; H. W. Oviatt, K. J. Shea, S. Kalluri, Y. Shi, W. H. Steier and L. R. Dalton, *Chem. Mater.*, 1995, **7**, 493; D. A. Loy, G. M. Jamison, B. M. Baugher, S. A. Myers, R. A. Assink and K. J. Shea, *Chem. Mater.*, 1996, **8**, 656.

9 H. W. Oviatt Jr, K. J. Shea and J. H. Small, *Chem. Mater.*, 1993, **5**, 943.

10 S. T. Hobson and K. J. Shea, *Chem. Mater.*, 1977, **9**, 616.

11 (*a*) R. J. P. Corriu, J. Moreau, P. Thépot and M. Wong Chi Man, *Chem. Mater.*, 1992, **4**, 1217; (*b*) 1996, **8**, 100; (*c*) *J. Mater. Chem.*, 1994, **4**, 987.

12 P. Audebert, P. Calas, G. Cerveau, R. J. P. Corriu and N. Costa, *J. Electroanal. Chem.*, 1994, **372**, 275; G. Cerveau, R. J. P. Corriu and N. Costa, *J. Non-Cryst. Solids.*, 993, **163**, 226; P. Audebert, G. Cerveau, R. J. P. Corriu and N. Costa, *J. Electroanal. Chem.*, 1996, **413**, 89.

13 (*a*) G. Cerveau, R. J. P. Corriu and C. Lepeytre, *J. Mater. Chem.*, 1995, **5**, 793; (*b*) *Chem. Mater.*, 1997, **9**, 2561.

14 P. J. Barri, S. W. Carr, D. Li Ou and A. C. Sullivan, *Chem. Mater.*, 1995, **7**, 265; S. W. Carr, M. Motavelli, D. Li Ou and A. C. Sullivan, *J. Mater. Chem.*, 1997, **7**, 865.

15 R. J. P. Corriu, P. Hesemann and G. Lanneau, *Chem. Commun.*, 1996, 1845.

16 P. Battioni, E. Cardin, M. Louloudi, B. Schöllhorn, G. A. Spyroulias, D. Mansuy and T. G. Traylor, *Chem. Commun.*, 1996, 2037.

17 J. P. Bezombes, C. Chuit, R. J. P. Corriu and C. Reyé, *J. Mater. Chem.*, 1998, **8**, 1749.

18 G. Cerveau, R. J. P. Corriu, C. Lepeytre and P. H. Mutin, *J. Mater. Chem.*, 1998, **8**, 2707.

19 G. Cerveau, R. J. P. Corriu, C. Fischmeister-Lepeytre and R. Combarieu, to be published.

20 E. A. Williams, *NMR Spectroscopy of Organosilicon Compounds*, ed. S Patai and Z. Rappoport, Wiley, New York, 1989, p. 511.

21 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.

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 D. F. Schriver, *The manipulation of Air-sensitive Compounds*, MacGraw-Hill, New York, 1969.

25 S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, London, 1982.

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