Sol–gel process: temperature effect on textural properties of a monophasic hybrid material

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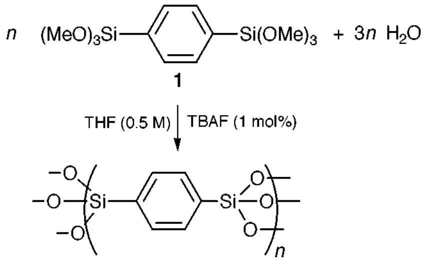
Monophasic hybrid materials with controlled porosity are obtained by varying the temperature, without change of the polycondensation at silicon atoms, confirming the kinetic control of formation of the solids.

The sol–gel processes which correspond to an inorganic polycondensation offer very wide possibilities since they allow the synthesis of materials from the molecular scale as illustrated in Scheme 1.[1] Hybrid organic–inorganic materials are one of the most attractive targets achievable by this chemistry.[2–8] Using the sol–gel route, it is possible to introduce a large variety of organic moieties into inorganic matrices, so leading to the possibility to tailor physico-chemical properties.[2] However, textural control of the solids obtained by the sol–gel route is difficult. For instance, it is known that the aging and drying of gels influence the textural properties for both silica and hybrid solids.[1,3] Furthermore, it has been observed that textural parameters (specific surface area, porosity, *etc.*) drastically change with the experimental conditions,[9–12] and some correlation with kinetic measurements in the first steps of the process have been performed.[1,13] These solids are considered as unstable[1] and reproducibility is often difficult to obtain from literature data since all the experimental details are of importance and are not always precisely reported. However, while *all* experiments are reproducible when a precise analytical procedure is *strictly* followed[9–12] predictability of the obtained product is not yet possible. We have shown previously that organic-inorganic materials are kinetically controlled solids with the properties of the solids being highly dependent on the chemical parameters such as nature and concentration of the catalyst,[9,10] nature of the solvent,[11] concentration of the precursor,[9] nature of the leaving group[11] and nature of the organic unit.[9,12] Here, we report the drastic influence of temperature which is a very important physical parameter for kinetic studies.

Adequate predictability will be attained when the parameters which control all the different steps of the sol–gel type synthesis are known (precursor → oligomers → polymers → colloids → sol → gel). The results presented here suggest that the polycondensation at silicon does not control the textural properties of the resulting solids.

The hydrolytic polycondensation of the molecular precursor 1,4-$C_6H_4[Si(OMe)_3]_2$ **1** (Scheme 1) has been studied in THF using tetrabutylammonium fluoride (TBAF) as catalyst at the −20, 3, 20 and 55 °C.† The entire experiment (addition of the reagents, gelation, aging) was performed at the given temperature. NMR and BET measurements were from the same sample.



Scheme 1

Considering the identification of the solids at the 'molecular level', ^{13}C and ^{29}Si CP MAS NMR spectra showed that no SiC bonds had been cleaved during reaction.[14,15] The ^{13}C CP MAS spectra showed the presence of the unmodified organic fragment along with some residual methoxy groups. For all solids the ^{29}Si CP MAS NMR spectra exhibited only T^1 [$C–Si(OR)_2(OSi)$], T^2 [$C–Si(OR)(OSi)_2$] and T^3 [$C–Si(OSi)_3$] substructures with no signal in the ranges δ −90 to −110 being observed. While CP MAS spectroscopy is not quantitative, it has been shown[12,16] that single pulse experiments (SPE) do not reveal any significant variation in relative peak intensities from CP MAS spectra if hydrogen atoms are absent in the direct vicinity of the studied nucleus. For the hybrid materials studied here, quantitative reliable ^{29}Si SPE MAS NMR spectra of gels obtained from **1** have been collected and compared to the ^{29}Si CP MAS NMR spectra.[12] The SPE MAS and CP MAS percentages found for the different T^x units were found to be similar. The percentages of the different substructures determined by deconvolution of CP MAS spectra (Table 1) gives a good estimation of the degree of polycondensation of the silsesquioxane network. We observe that the temperature of the hydrolysis–polycondensation reaction has no influence on the polycondensation around silicon, the relative contributions of the T^x units being very similar whatever the temperature.

Table 1 ^{29}Si CP MAS NMR data for xerogels obtained from **1**

		Site population[a] (%)			Level of condensation
Xerogel	T/°C	T^1	T^2	T^3	(%)
1a	−20	18	49	33	71
1b	+3	19	53	28	69
1c	+20	16	64	20	67
1d	+55	18	42	40	74

[a] Obtained by deconvolution of ^{29}Si CP MAS NMR spectra.

By contrast, specific surface areas and porosities of the xerogels appeared to be very sensitive to temperature. They were determined by 35-point adsorption–desorption isotherm plot measurements[17] and evaluated using the BET equation.[18] The determination of the porous volume by the BJH method[19,20] and evaluation of the microporous volume by the analysis of the *t*-plot diagram were performed in each case. The values of specific surface areas were very high whatever the temperature being in the range 900–1300 $m^2 g^{-1}$. The main influence of the temperature was observed in the porosity of the gels. The shape of the curves of the adsorption–desorption isotherms depended strongly on the temperature (Fig. 1). At low temperature [−20 °C (**1a**) and 3 °C(**1b**)], the isotherms were of type I [Fig. 1(a) and (b)] indicating a largely microporous solid with a low mesoporous contribution, though vestiges of hysteresis loops characteristic of capillary filling of mesopores were evident. The microporous volume represented 40–55% of total porous volume. The mesopores did not exhibit a narrow pore size

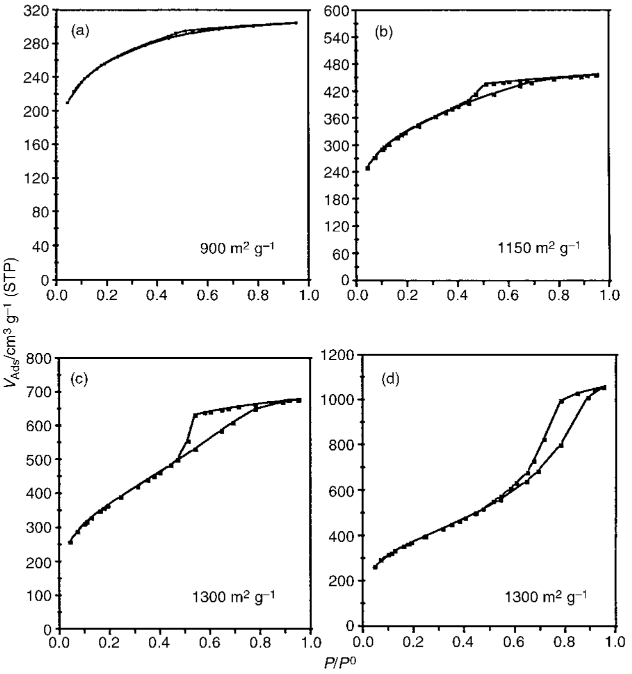


Fig. 1 N_2 adsorption–desorption isotherms of xerogels at −20 (a), 3 (b), 20 (c) and 55 °C (d).

distribution (20–120 Å). When the temperature was raised to +20 °C (**1c**), the isotherm became characteristic of type IV [Fig. 1(c)]. The microporous volume was 10% and the mesopore size lay in the range 20–120 Å. At +55 °C (**1d**), only 5% of micropores were present and mesopores showed a narrow pore size distribution (55–70 Å) characteristic of isotherms of type IV [Fig. 1(d)]. The results presented here thus show the drastic influence of temperature on the texture of the xerogels variation of which allows control of the porosity of the materials. At low temperatures, solids were mainly microporous whereas at higher temperature mesoporous solids with narrow pore size distribution were obtained.

In summary, this work confirms that hybrid materials obtained by hydrolytic polycondensation are under kinetic control. The temperature appears to be a fundamental parameter which allows the control of the textural properties of the solids. However, the drastic change observed in the porosity is not correlated with any change in the degree of polycondensation at silicon which remains insensitive to the temperature. This fact suggests that textural properties such as porosity are not controlled by the process of polycondensation at silicon.

Notes and references

† *Experimental procedure*: the preparation of gels was carried out according to the following general procedure. The precursor **1** was analytically pure (Anal. Calc. for $C_{12}H_{22}O_6Si_2$: C, 45.26; H, 6.96; Si, 17.64. Found: C, 44.88; H, 6.91; Si, 17.41%). The preparation of xerogel **1a** is given as an example. To 2.86 g (9 mmol) of **1** in 9 ml of dry (distilled over Na) THF (3 µmol H_2O/ml measured by the Karl Fisher method) was added at −20 °C a solution in 8.40 ml of dry THF of 90 µl (90 µmol) of TBAF (in THF, $[F^-]$ = 1 mol l^{-1} as measured by electrochemistry[21]) and 486 µl (27 mmol) of H_2O. The mixture was kept at −20 °C and after 90 min a monolithic gel had formed. After further aging for 6 days at −20 °C, the solid was collected, ground and washed twice with ethanol, acetone and diethyl ether. The resulting solid was dried at 120 °C *in vacuo* for 3 h yielding 1.70 g of a white powder **1a**. CP MAS NMR: ^{13}C, δ 133.6 (aromatic C), 50.7 (residual OMe); ^{29}Si, δ −62.0 (T^1), −69.5 (T^2), −78.0 (T^3).

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