Organic–inorganic hybrid silica. Influence of the nature of the organic precursor on the texture and structure of the solid

Geneviève Cerveau, Robert J.P. Corriu *, Cédric Lepeytre

Laboratoire de Chimie Moléculaire et Organisation du Solide, Université Montpellier II, Case Courrier 007, Place E. Bataillon, F-34095 Montpellier Cedex 5, France

Abstract

This paper shows that the properties of hybrid organic–inorganic solids are kinetically controlled: All parameters able to modify the kinetics of the hydrolysis–polycondensation process (nature of the reaction used, concentration of reagents, solvent, functionality at silicon, catalyst, etc.) are of importance for both the physical and chemical properties of the solid. Hybrid gels obtained from hydrolysis of 1,4-bis(trihydrosilyl)phenylene compounds have been studied. All the kinetic parameters tested control the reactivity of the phenyl groups towards $Cr(CO)_6$, the hydrophilicity, the specific surface area and even the macroscopic aspect of the solids obtained by hydrolytic polycondensation. © 1997 Elsevier Science B.V.

Organometallic chemists have succeeded in finding chemical ways for binding most metals to carbon, thus obtaining polymetallic species and controlling many chemical processes involving carbon units and metallic centres. Besides the development of catalysis, one of the goals for organometallic chemistry nowadays is the synthesis of materials or, in other words, the elaboration of solids with specific properties. Until now the elaboration of materials has been performed using the methods of solid state chemistry with only a few exceptions (Yajima [1] and Sol-Gel processes [2] for instance) where molecular precursors were used.

In view of this, organic–inorganic hybrid solids constitute a very attractive field of investigation for organometallic chemists [3]. This class of solids encompasses inorganic solids as fillers in organic polymers, as well as organic molecules included in inorganic networks.

We have focused our interest on the case of hybrid solids in which organic molecules are bound to silica by at least two covalent bonds. These solids are obtained by hydrolytic polycondensation which permits, in one step, a highly crosslinked solid to be obtained from a molecular precursor (Scheme 1).

Studies have been performed on different systems studying specific surface area, structure and chemical reactivity of the solids obtained [4].

In a previous paper, we have reported the drastic effect of the chemical structure of the organic moiety on the properties of the solid [5]. The rigid systems give hydrophilic materials with high specific surface area in which the phenyl groups are not accessible for chemical reactions. In contrast, the flexible systems are hydrophobic; they do not exhibit any specific surface area but they react easily offering possible complexation of a $Cr(CO)_3$ moiety.

In this paper, we show that the structure of the organic moiety is not the only factor which controls the structure of the solid: all the parameters which can influence the kinetics of polycondensation used for building up the solid are of importance.

An alternative route to the hydrolysis of Si(OR)bonds is the hydrolytic condensation of Si–H of trihydrosilanes [6]. The interest in this method is to avoid the formation of alcohols or acids, since the leaving group is removed as

* Corresponding author. Tel.: +33 4 67143801; Fax: +33 4 67143888.

$$(RO)_3Si \underline{\quad\quad\quad} Si(OR)_3$$
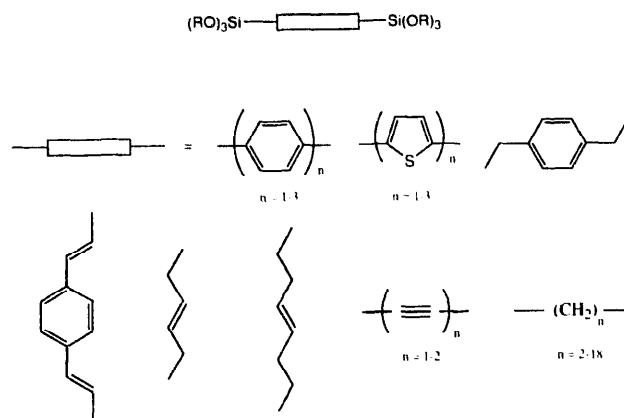
Scheme 1.

hydrogen gas. We report here our preliminary results on the properties (chemical reactivity, specific surface area, hydrophilicity) of organic–inorganic hybrid silica gels obtained from precursors 1 and 2.
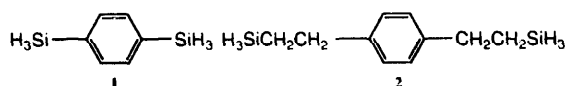
The hydrolysis of the precursors rigid 1,4-bis(trihydrosilyl) benzene (1) and flexible 1,4-bis(trihydrosilylethyl) benzene (2) [1] were performed in the presence of two types of catalyst: nucleophilic (tetrabutylammonium fluoride TBAF) and the transition metal catalyst [Cl Rh (PPh$_3$)$_3$] [6] (Eq. 1).
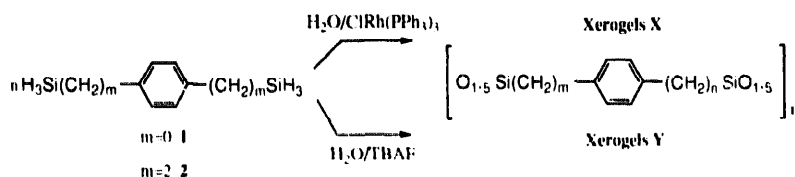
In both cases the reactions were performed in freshly distilled THF with two concentrations of the precursor (0.5 and 1 M) in the presence of 1 mol% of catalyst. The reagents were mixed at 0°C because of the evolution of hydrogen and the mixture was then allowed to warm to room temperature. Colourless gels are formed after various gel times. After ageing during 7 days, the gels were filtered and washed as usual and then dried in vacuo at 120°C during 3 h. The physical properties of the gels obtained from 1 and 2 are reported in Table 1.

The conservation of the structure of the precursor inside the solid and the absence of cleavage of the Si–C bond during the gelation process were established by solid state ^{13}C- and ^{29}Si-NMR. ^{13}C-NMR exhibits resonances corresponding to the organic moieties respectively at 133 ppm (aromatic) for gels obtained from 1 and at 14 and 28 ppm (CH$_2$) and 128 and 143 ppm (aromatic) starting from 2. No [29]Si resonances in the region of −100 ppm which would correspond to SiO$_4$ units are detected. ^{29}Si-NMR spectra of the xerogels are reported in Table 2.

The xerogels obtained with the rhodium catalysis appeared to be partially cross-linked materials containing residual Si-H bonds. Major resonances at −45 ppm (Table 2, entries 1 and 2) corresponding to SiC(H)O$_2$ substructures observed in the case of X1 and X'1 are indicative of an Si–H containing material. In the case of X2 (Table 2, entry 5) the two resonances observed at −34 and −19 ppm corresponding to SiC(H)O$_2$ and SiC(H) (OH) O substructures are indicative of a very low degree of polycondensation [6]. These peak assignments have been confirmed by use of solid state ^{29}Si-NMR using high power proton decoupling with a recycle delay time of 10 s. For example, the application of this technique in the case of X'1 results in an increase in intensity of the signals at −60, −68 and −76 ppm with

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[1] Compound 2 was obtained by reduction with LiAlH$_4$ of the 1,4-bis(trimethoxysilylethyl) benzene 4.

Table 1
Physical properties of xerogel obtained by hydrolysis of 1 and 2

Entry	Precursor	Precursor concentration (M)	Catalyst	Gel time (h)	Xerogel	Surface area[a] ($m^2 g^{-1}$)	$E^b_{0,6}$ (%)
1	1	0.5	ClRh(PPh₃)₃	86	X1	54	2.5
2	1	1	ClRh(PPh₃)₃	23	X'1	360	5
3	1	0.5	TBAF	5	Y1	931	10
4	1	1	TBAF	0.2[c]	Y'1	1200	16
5	2	0.5	ClRh(PPh₃)₃	0.5	X2	100	2.5
6	2	1	ClRh(PPh₃)₃	0.33	X'2	518	1.5
7	2	0.5	TBAF	0.58	Y2	362	2
8	2	1	TBAF	0.41	Y'2	494	2.5

[a] BET surface area from multipoint analysis of N_2 adsorption isotherm.
[b] % weight increase in a 60% humidity atmosphere at 25°C.
[c] Temperature = −15°C.

respect to those at −25 and −45 ppm. The other resonances observed with xerogel X and reported in Table 2 are very weak and minor.

In contrast the xerogels Y obtained from fluoride ion catalysis appeared to be highly condensed hybrid siloxane networks. The three resonances at −77, −70 and −61 ppm corresponding to $SiCO_3$ units are major and have high intensities in the case of Y1 and Y'1 (Table 2, entries 3 and 4). The same feature is observed for Y2 and Y'2 with a strong resonance at −65 ppm attributable to $SiCO_3$ (Table 2, entries 7 and 8) [7]. The other resonances reported in Table 2 for xerogel Y are minor.

FTIR spectra are in good agreement with these results. The spectra of xerogel X presented an intense Si–H vibration at 2176 cm⁻¹ whereas in the case of Y a weak Si–H absorption at 2158 cm⁻¹ was observed.

All the physical properties of the xerogels X and Y (gelation time, specific surface area, hydrophilicity and even the physical appearance) as well as the chemical reactivity are highly dependent on the parameters controlling the kinetics of the hydrolysis–polycondensation process:

(i) Gelation time. Shorter gel times were observed with flexible precursor 2 whatever the catalyst, except in the case of 1 with TBAF catalysis, (Table 1, entry 4). In this case the reaction was strongly exothermic, so the reagents were mixed at −15°C and the solution was allowed to warm up at RT once hydrogen evolution had decreased.

(ii) Specific surface area. Xerogels X resulting from rhodium catalyst hydrolysis present low to moderate specific surface areas starting from either 1 or 2 (Table 1, entries 1, 2, 5, 6). Interestingly, increasing the concentration of the precursor induces an increase in the surface area. However when the hydrolysis was catalysed by fluoride ion, a very high surface area ($\approx$ 1000 $m^2 g^{-1}$) was observed for Y1 and Y'1 (Table 1, entries 3, 4) whereas 362 and 494 $m^2 g^{-1}$ were found for Y2 and Y'2 (Table 1, entries 7, 8). In the case of fluoride ion catalysis, the concentration of the precursor has less influence on the surface area.

(iii) Hydrophilicity. The xerogels exhibited a low affinity for water: increases in weight (in a 60% humidity atmosphere at 25°C) are reported in Table 1. The hydrophobic character observed for gels X (Table 1, entries 1, 2, 5, 6) is in agreement with Si–H bonds remaining at the surface of the material. Gels obtained from fluoride ion catalysis were more hydrophilic in the case of Y1 (Table 1, entries 3, 4) and hydrophobic for Y2 (Table 1, entries 7, 8). Such a result was previously observed when the corresponding bis(trimethoxy)silyl derivatives were hydrolysed [5].

Table 2
²⁹Si Solid state NMR spectra of xerogels X and Y[a]

Entry	Xerogel	δ ²⁹Si					
		SiC(H)(OH)₂	SiC(H)(OH)O	SiC(H)O₂	SiC(OH)₂O	SiC(OH)O₂	SiCO₃
1	X1	−25		**−45**	−60		**−76**
2	X'1	−25		**−45**	−60	−68	**−76**
3	Y1	−25		−46	**−61**	**−70**	**−77**
4	Y'1		−36	−46	**−61**	**−69**	**−77**
5	X2		**−19**	−34		−58	**−64**
6	X'2		**−19**	−33		−57	**−65**
7	Y2			−33			**−65**
8	Y'2		−20	−34	−47	−56	**−66**

[a] Major resonances are in bold characters.

Table 3
IR and ^{13}C-NMR data of xerogels after reaction with Cr(CO)$_6$

Entry	Xerogel	IR	δ^{13}C				Degree of complexation (%)	
		νCO	CO	Non complexed aromatic	Complexed aromatic	CH$_2$	EDS Anal.	Elem.
1	X1	no bands	no signals	133	no signals	–	–	–
2	X'1	1981 and 1915 (w)	a	133	a	–	16	8
3	Y1	1970 and 1880 (w)	233	133	95	–	30	10
4	Y'1	1981 and 1910 (w)	–	–	–	–	10	–
5	X2	1970 and 1880 (w)	233	128 and 143	93 and 115	15 and 28	28	22
6	X'2	1970 and 1880 (w)	a	128 and 143	a	18 and 28	10	7
7	Y2	1970 and 1880 (vs)	233	128 and 143	95 and 115	15 and 28	75	62
8	Y'2	1970 and 1988 (vs)	233	128 and 143	95 and 115	15 and 28	60	44

^{a} Not detected at NMR scale.
(w), weak; (vs), very strong.

(iv) Physical appearance. The aspect of the solids obtained from **1** and **2** is totally different in the case of rhodium catalysis: from **1** the xerogels **X1** (Table 1, entries 1, 2) appear as finely divided powders whereas the gels **X2** obtained from **2** (Table 1, entries 5, 6) are very hard solids which cannot be transformed into fine powders even under pressure. With fluoride ion catalysis, gels **Y1** and **Y2** (Table 1, entries 3, 4, 7, 8) are powders in both cases.

(v) Chemical reactivity. In order to study the solid arrangement as a function of the molecular structure, we used the complexation of aromatic groups with Cr(CO)$_6$ to test the accessibility of the phenyl groups attached to the silica network in xerogels **X** and **Y** [5] (Eq. 2).

The reactions were performed in a refluxing mixture of nBu$_2$O/THF (4/1) under argon during 65 h. Yellow-greenish powders were isolated and analysed by the usual spectral techniques.

FTIR spectra and ^{13}C-NMR spectra showed the presence or absence of complexation of aromatic groups by Cr(CO)$_3$. The results are reported in Table 3. Absorption bands at about 1970 and 1880 cm^{-1} indicate the presence of carbonyl groups. Furthermore, the emergence of new ^{13}C-NMR signals at 233 ppm (carbonyl) and at 95 ppm (complexed aromatic) for **Y1** and 95 and 115 ppm (complexed aromatic) for **Y2** (Table 3, entries 4, 5, 7, 8) revealed a partial complexation reaction. In the case of entries 2 and 6, very weak νCO bands are observed and no signal corresponding to CO ligands and complexed aromatics could be detected by NMR. The degree of complexation was determined by elemental analysis and by EDS (Energy Dispersive Spectrometry) which provide data in good agreement. From these results, reported in Table 3, it is obvious that the organization of the amorphous hybrid solids is highly dependent on the kinetic parameters controlling the hydrolysis–polycondensation process. They include the concentration of reagents, solvent, catalyst and the nature and geometry of the organic moiety. When the rhodium catalyst is used, phenyl groups are not easily accessible for complexation: no reaction occurs with **X1** (Table 3, entry 1) and only a poor degree of complexation is observed in other cases (Table 3, entries 2, 5, 6).

In the case of fluoride ion catalysis, a drastic difference in the reactivity of **Y1** and **Y2** is observed. **Y1** (obtained from rigid precursor **1**) reacts weakly with Cr(CO)$_6$, whereas large amounts of complexation are obtained with **Y2** (flexible starting precursor **2**) (Table 3, entries 3, 7, 8). Similar results have been previously observed when the corresponding methoxy derivatives **3** and **4** were employed [5,8].

It was shown that starting from **3**, no complexation was observed, whereas from **4**, 52–70% of complexation were detected: the arrangement of the organic units in the silica matrix depends on the structure of the organic precursor (rigid or flexible).

In conclusion, the results reported here show that the structure of the organic moiety is only one of the parameters influencing the organization of the hybrid solid. All the parameters able to modify the kinetics of the substitution reactions taking place at silicon during the polycondensation process control the formation of the solid and are of importance for the texture of the hybrid material. Changing the functionality at silicon, the nature of the organic moiety, the concentration of species, or the catalyst, modifies drastically the structure of the hybrid solid.

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