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Generation of Microporosity in a Hybrid Material. Access to Pillared Amorphous Organosilicate

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The potentiality of a new route for creating a controlled porosity in an hybrid xerogel was investigated using the selective removal of the rigid 1,4-bis(ethynyl)benzene group in an hybrid xerogel of the general formula $\{[(O)_{1.5}Si-C\equiv C-C_6H_4-C\equiv C-Si(O)_{1.5}]_x[(O)_{1.5}Si-C_6H_4-C_6H_4-Si(O)_{1.5}]_{1-x}\}$. Preparation of these xerogels was achieved by HCl-catalyzed sol−gel copolycondensation of precursor **A**, 1,4-bis(trimethoxysilylethynyl)benzene, mixed with various amount of precursor **B**, 4,4′-bis(trimethoxysilyl)biphenyl, in THF ((A:B) = (100:0), (80:20), (60:40), (40:60), (20:80) and (0:100). Elimination of the 1,4-bis(ethynyl)benzene group of **A** was achieved by a selective and mild chemical treatment that prevents the elimination of the biphenylene group introduced by precursor **B**. The porosity of the materials before and after chemical treatment was measured by helium pycnometry, water adsorption, and N_2 and Ar porosimetry, this porosity mainly varies in relation to the initial (**A**:**B**) ratio. A microporous material with high hydrophobic surface (mean pore diameter $\phi < 10$ Å) is obtained when high proportions of **B** are used. Lowering the proportion of **B** mainly leads to an increasing proportion of mesopores (mean pore diameter $10 < \phi < 200$ Å) that results from a percolation of the voids and the reorganization of the silica network. As a side reaction, the chemical treatment promotes an increase in the level of polycondensation. Interestingly, the porosity of the final material is consistent with a random polycondensation of the precursors during the gelation step.

Introduction

For a material, the control of the porosity is one of the most important properties that determine its usefulness.[1] On the other hand, hybrid organic−inorganic silica-based materials are attractive materials due to the possibility of combining the properties of organic moieties and inorganic frameworks. [2−12] By making an analogy with the mineral oxides such as zeolithes,[13] a controlled porosity for these hybrid solids may open the development of their physical and chemical properties for application like selective separation, complexation, catalyst, etc....[14] They are prepared under mild conditions by sol−gel polycondensation of precursors such as $R-Si(OR)_3$ or $Si(OR)_3-R-Si(OR)_3$. In the latter case the organic group is incorporated uniformly in a silica matrix. The material's porosity is closely related to both the physicochemical properties of the group R and the experimental conditions used during the sol−gel process. It corresponds to a kinetic control of the porosity that cannot be modified once it is formed. For example, hybrid xerogels are mostly microporous materials for R equal to $-(C_6H_4)_n-$ ($n = 1-3$),[15] $C\equiv C$[16] or $C\equiv C-(CH_2)_n-C\equiv C$ ($n = 0-2$).[17,18] In contrast, nonporous materials are obtained with $C\equiv C-(CH_2)_n-C\equiv C$ ($n = 4-8$),[18] $-(CH_2)_n-$ ($n = 2-8$),[19,20] or $C\equiv C-(C_6H_4)-C\equiv C$.[21,22] The control of the porosity of these materials can be carried out in two ways by preparing thin films[23] or by using supercritical carbon dioxide as solvent.[24]

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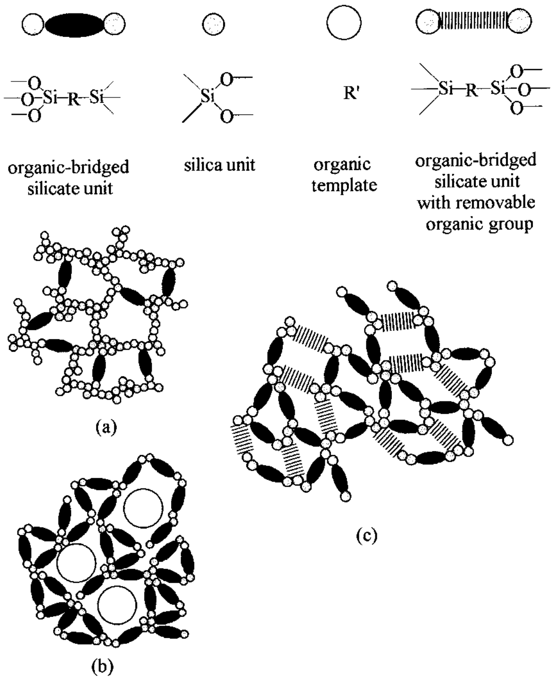
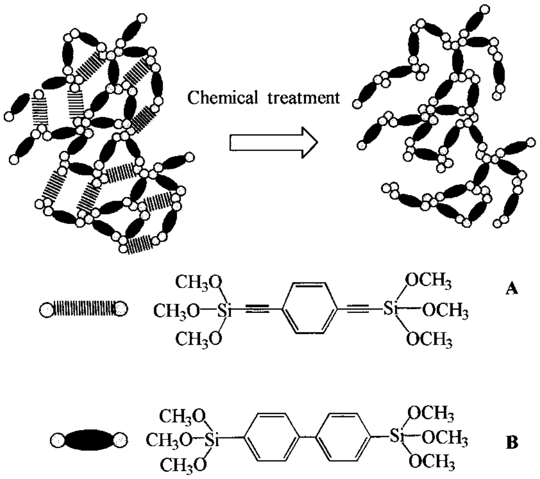
Scheme 1



From a general point of view, the control of this amorphous hybrid's porosity can be achieved following three main approaches. For example, copolycondensation of $(RO)_3Si-R-Si(OR)_3$ with tetraalkoxysilane is conceivable (Scheme 1a).[8,21,22] This can also be achieved in the presence of an organic templating agent, which is removed subsequently by washing, or by using an oxidative treatment (Scheme 1b).[8] The last possibility that we considered here is the copolycondensation of two precursors followed by a selective removal of one of the spacers as shown in Scheme 1c. In the case of crystallized phosphonate, this last approach was successfully achieved by selective hydrolysis of diphosphonate and diphosphate resulting in microporous phosphonate.[25]

This route requires a chemical tool to selectively remove one of the two organic groups. The thermal oxidation generally used in such cases cannot be used here because of its lack of selectivity.[8,26] We have recently reported the use of a chemical treatment to achieve the elimination of an organic spacer of an hybrid xerogel of general formula $(O)_{1.5}Si-C\equiv C-R-C\equiv C-Si(O)_{1.5}$, R = $-C_6H_4-$ or $-(CH_2)_n-$ ($n = 2-4$). An excess of $MeOH/H_2O$ and NH_4F (2%) as catalyst allows cleavage of the $Si-C_{sp}$ bond, and the organic spacer is removed and recovered in high yield.[17,18,21,22,27−29] Therefore, it seemed possible by using this approach to create a porosity in an hybrid xerogel elaborated with two precursors: one containing a $Si-C_{sp}$ bond and the other one with a non hydrolyzable $Si-C_{sp^2}$ bond. To explore this approach, we chose to copolycondense two bis(trimethoxysilyl) precursors having similar size and rigidity: 1,4-bis(trimethoxysilylethynyl)benzene (**A**) and the 4,4′-bis(trimethoxysilyl)biphenyl (**B**) (Scheme 2). They are both rodlike molecules containing aryl groups, and their geometries are similar, the Si···Si distance being 11.5 Å for **A** and 10.8 Å for **B**. In this paper we present the preparation and characterization of hybrid xerogels obtained by copolycondensing precursors **A** and **B** in different molar ratios. The selective removal of the 1,4-bis(ethynyl)benzene group introduced by the precursor **A** was attempted by a chemical treatment similar to the one used in previous studies.[18,21,29] We wish to report how this selective chemical treatment allowed us to prepare hybrid xerogels with various porosities closely related to the initial **A**:**B** ratio. We have reported that complete elimination of the organic part of this kind of hybrid material led to a complete reorganization of the silica network;[30] the present results argue for a limitation of this phenomenon if some organic groups are kept in the material.

Scheme 2



Results

Preparation of the Precursors. Precursor **A**, 1,4-bis(trimethoxysilylethynyl)benzene, was prepared following the synthesis pathway previously reported.[22] Precursor **B**, 4,4′-bis(trimethoxysilyl)biphenyl, was prepared by direct silylation of 4,4′-dibromobiphenyl with chlorotrimethoxysilane in the presence of magnesium.[16,22,31]

Preparation and Chemical Treatment of the Hybrid Xerogels. Hydrolysis of the precursors was performed by sol−gel process in order to obtain the xerogel $\mathbf{H}_n$, where n refers to the molar percentage of **A** used for the preparation of the xerogel (n = 100, 80, 60, 40, 20 and 0). This hydrolytic copolycondensation ideally corresponds to step 1 of eq 1 where all the methoxy groups are hydrolyzed to form siloxane bridges.

Preliminary experiments have demonstrated that in the absence of catalyst, gelation of precursor **A** requires a few minutes (5−10) while gelation of **B** takes several days (7−10). Using HCl as a catalyst,[7,32] it was possible to obtain similar gelation times for both precursors. This

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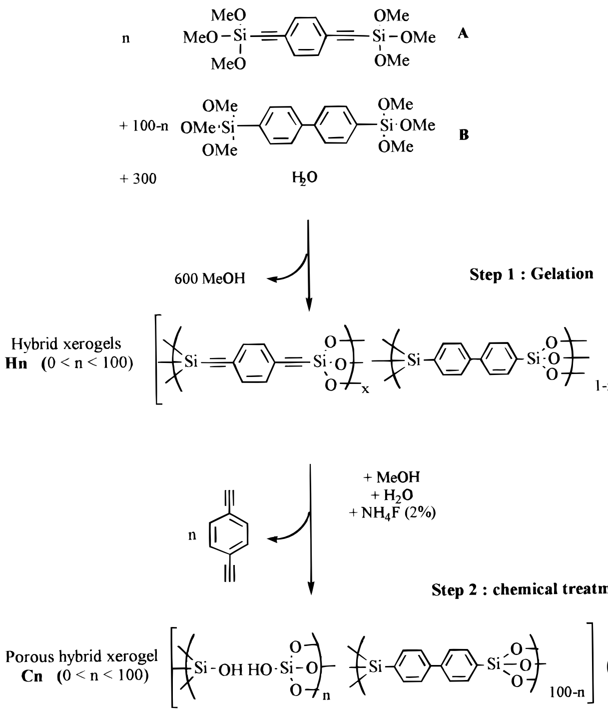
Table 1. Elemental Analyses of Xerogels H_n and C_n

	before chemical treatment			after chemical treatment	
	calcd[a]	found		calcd[b]	found
$\mathbf{H_{100}}$	$C_{10}H_4Si_2O_3$	$C_{10.8}H_{10.3}Si_2O_{3.9}$	$\mathbf{C_{100}}$	$H_2Si_2O_5$	$C_{0.7}H_{2.5}Si_2O_{4.9}$
$\mathbf{H_{80}}$	$C_{10.4}H_{4.8}Si_2O_3$	$C_{11.5}H_{9.0}Si_2O_{4.3}$	$\mathbf{C_{80}}$	$C_{2.4}H_{4.6}Si_2O_{4.6}$	$C_{2.8}H_{4.7}Si_2O_{4.9}$
$\mathbf{H_{60}}$	$C_{10.8}H_{5.6}Si_2O_3$	$C_{12.2}H_{12.1}Si_2O_{4.5}$	$\mathbf{C_{60}}$	$C_{4.8}H_{4.4}Si_2O_{4.8}$	$C_{5.3}H_{5.4}Si_2O_{4.5}$
$\mathbf{H_{40}}$	$C_{11.2}H_{6.4}Si_2O_3$	$C_{13.6}H_{12.3}Si_2O_{4.5}$	$\mathbf{C_{40}}$	$C_{7.2}H_{5.6}Si_2O_{3.8}$	$C_{8.6}H_{9.3}Si_2O_{4.4}$
$\mathbf{H_{20}}$	$C_{11.6}H_{11.6}\ Si_2O_3$	$C_{13.8}H_{14.1}Si_2O_{4.4}$	$\mathbf{C_{20}}$	$C_{10.0}H_{6.8}Si_2O_{3.4}$	$C_{11.5}H_{11.9}Si_2O_{4.2}$
$\mathbf{H_0}$	$C_{12}H_8Si_2O_3$	$C_{12.4}H_{11.2}Si_2O_{4.5}$	$\mathbf{C_0}$	$C_{12}H_8Si_2O_3$	$C_{12.1}H_{9.8}Si_2O_{3.8}$

[a] Assuming a total polycondensation. [b] Assuming a total elimination of the bis(1,4-ethynyl)phenylene group.

was achieved at room temperature with THF as solvent. The following molar ratios were used: precursor:water: solvent:HCl = 1:3:12:1 × 10^{-2}. Gelation occurred within 10 min for **A** and within 600 min for **B**. These conditions were used for the copolycondensation of the (**A:B**) precursor mixture to prepare the hybrid xerogels $\mathbf{H}_{\boldsymbol{n}}$. Hydrolysis and polycondensation led to gelation in a few minutes. The resulting gels were allowed to stand 8 days for aging at room temperature for further condensation. They were then powdered, washed with solvents, and dried in a vacuum at room temperature. The mixture of solvents recovered from the filtration was evaporated in order to check the presence of soluble residues. Only traces of solid precursors, less than 1% in weight, were recovered. The yields for these preparations are slightly higher than 100% due to residual Si−OR (R = H or Me) or adsorbed solvent (water or organic solvent).



(1)

The chemical treatment of the xerogel $\mathbf{H}_{\boldsymbol{n}}$ was performed using a mixture of MeOH, H_2O and NH_4F as a catalyst at 60−65 °C for 4 days.[18,22] After treatment the solid residue was filtered and washed with organic solvent in order to separate the soluble organic byproduct from the corresponding hybrid xerogels $\mathbf{C}_{\boldsymbol{n}}$. The crude 1,4-bis(ethynyl)benzene was quantitatively recovered in all cases (step 2 of eq 1).

Table 2. Assignment of the ^{29}Si NMR Signals for H_n and C_n

T^n and Q^n units		for precursor **A**	for precursor **B**	silica
T^0	C−**Si**(OR)$_3$	$T_A{}^0$ − 69.5	$T_B{}^0$ − 56.1	
T^1	C−**Si**(OR)$_2$(OSi)	$T_A{}^1$ − 78.8	$T_B{}^1$ − 59.0	
T^2	C−**Si**(OR)(OSi)$_2$	$T_A{}^2$ − 87.2	$T_B{}^2$ − 65.0	
T^3	C−**Si**(OSi)$_3$	$T_A{}^3$ − 96.6	$T_B{}^3$ − 77.0	
Q^2	**Si**(OR)$_2$(OSi)$_2$			−90.7
Q^3	**Si**(OR)(OSi)$_3$			−100.4
Q^4	**Si**(OSi)$_4$			−110.8

Composition and Structure of the Material before and after Chemical Treatment. Elemental analyses of the xerogels before and after chemical treatment leads to the formulas presented in Table 1. Oxygen content measurements in such samples were not possible, and it was estimated by difference with the analysis of the other elements. For the hybrid xerogels $\mathbf{H}_{\boldsymbol{n}}$, the amounts of hydrogen, carbon, and oxygen are higher than expected for a complete hydrolysis of the precursor. This was due to traces of solvent and mainly the Si−OMe or Si−OH function (confirmation of this will be found in the ^{29}Si NMR data section).

For the xerogels obtained after chemical treatment, a formulation was calculated on the basis of a complete removal of the 1,4-bis(ethynyl)phenylene group and the formation of a Si−OH group according to the previous results that we have reported.[21,22] The experimental values agree with those calculated as presented in Table 1. The slight excess of carbon is attributed to the presence of residual organic groups (< 5%) or adsorbed solvent.

^{29}Si CP MAS NMR analyses were performed on the samples before and after chemical treatment in order to evaluate the local environment of the silicon atom which is related to the signal's chemical shift. CP MAS is a convenient sequence for solid state analysis since it requires a rather short acquisition time. However, the intensity of the signal is closely dependent on both the distance to and the number of hydrogen atoms in the silicon atom's environment; therefore, the peak intensity does not accurately represents the population in the sample, and the information is mainly qualitative.

Before the chemical treatment, we observed T^n signals characteristic of silicon atoms linked to three oxygen atoms and one C_{sp} atom. They were attributed by reference to the literature and also by comparison with the hybrid xerogel $\mathbf{H_{100}}$ and $\mathbf{H_0}$ prepared with pure **A** or pure **B** (Table 2).[33] The absence of Q^n signals shows that no cleavage of the organic part occurred during the gel formation. The hybrid xerogels $\mathbf{H_{80-20}}$ present the $T_{\mathbf{A}}{}^n$ and $T_{\mathbf{B}}{}^n$ signals of both precursor **A** and **B**, but the

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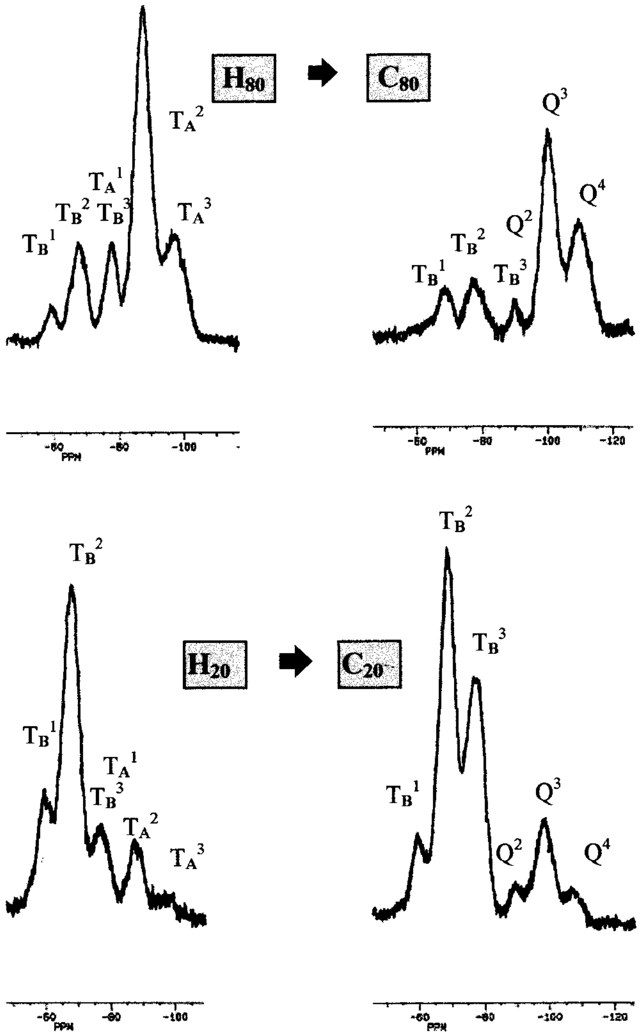

Figure 1. Examples of ^{29}Si CP MAS NMR spectra of hybrids before and after chemical treatment.

$T_{\mathbf{A}}^{1}$ signal and the $T_{\mathbf{B}}^{3}$ signal are superposed (Figure 1). Despite their qualitative nature some comparisons can be attempted because of the similarity of the $\mathbf{H}_{\boldsymbol{n}}$ materials. Accordingly, the intensity of the $T_{\mathbf{A}}^{n}$ and $T_{\mathbf{B}}^{n}$ signals increases with the molar ratio of the corresponding precursor. The $T_{\mathbf{A}}^{2}$ and $T_{\mathbf{B}}^{2}$ signals always have the highest intensity among the corresponding $\mathbf{T_A}^{n}$ and $\mathbf{T_B}^{n}$ signals. This result is consistent with the elemental analysis and allows us to describe the siloxane network as cross-linked siloxane chains bridged by the organic moiety with an average of one remaining uncondensed function per silicon atom.

After chemical treatment, instead of the $T_{\mathbf{A}}^{n}$ signals, we observed Q^n signals resulting from the hydrolysis of the Si$-$C$_{sp}$ bond. Starting from $T_{\mathbf{A}}^{n}$ units with $n = 1-3$, hydrolysis should lead to the formation of Q^n units with $n = 1-3$ in the absence of any other reaction. In contrast, we found mainly Q^3 and Q^4, with no Q^1 and a low intensity for the Q^2 signals. We assumed that the Q^1 signal is hidden by the $T_{\mathbf{B}}^{3}$ resonance. Therefore, this indicates that, aside from the Si$-$C$_{sp}$ hydrolysis, chemical treatment promotes the hydrolysis and/or polycondensation of Si$-$OMe or Si$-$OH functions.

Table 3. Characteristics of the Porosity of Xerogels $\mathbf{H}_{\boldsymbol{n}}$ and $\mathbf{C}_{\boldsymbol{n}}$

	microporous volume (cm^3 g^{-1}) in N$_2$ (in *Ar*)	single point surface area (m^2 g^{-1}) in N$_2$ (in *Ar*)	mean pore diameter (Å)	density (g cm^{-3})
$\mathbf{H_{100}}$		<10		1.38
$\mathbf{C_{100}}$	0.01	650	50	2.09
$\mathbf{H_{80}}$		<10		1.46
$\mathbf{C_{80}}$	0.03 *(0.07)*	1050 *(1220)*	<40	1.72
$\mathbf{H_{60}}$		<10		1.33
$\mathbf{C_{60}}$	0.30 *(0.27)*	1270 *(1150)*	<30	1.56
$\mathbf{H_{40}}$		<10		1.43
$\mathbf{C_{40}}$	0.31 *(0.25)*	940 *(740)*	<30	
$\mathbf{H_{20}}$		<10		1.41
$\mathbf{C_{20}}$	0.28 *(0.20)*	830 *(872)*	<20	1.43
$\mathbf{H_{0}}$		<10		1.32
$\mathbf{C_{0}}$		<10		1.45

The chemical treatment also induces modifications of the $T_{\mathbf{B}}^{n}$ signals leading to an increase of the $T_{\mathbf{B}}^{3}$ signal intensity with a simultaneous decrease of the $T_{\mathbf{B}}^{1}$ signal intensity. Despite the qualitative aspect of these measurements, a comparison of the signals before and after hydrolysis can be attempted in those cases since we are only looking to the variation of the signals' intensities. This facts demonstrate that the chemical treatment also promote the polycondensation of the remaining $T_{\mathbf{B}}^{n}$ units.

^{13}C CP MAS NMR spectroscopy was also performed on $\mathbf{H}_{\boldsymbol{n}}$. Signals at 50 and 60 ppm arise from the presence of residual $-$O$-$CH$_3$ groups in agreement with the elemental analyses. Signals related to the C$_{sp}$ carbon atom of the acetylenic moiety at $\delta = 102$ and 90 ppm were present in all the **A**-containing xerogels' spectra along with signals at 132 and 123 ppm due to the aromatic ring of this precursor. The chemical treatment leads to their disappearance and confirms the total elimination of 1,4-bis(ethynyl)benzene. Additional signals around 142, 135, and 128 ppm arise from the biphenylene group and are observed in $\mathbf{H}_{\boldsymbol{n}}$ and $\mathbf{C}_{\boldsymbol{n}}$.

Characterization of the Porosity. *Helium Pycnometry.* For the xerogels $\mathbf{H_{100}}$ and $\mathbf{H_0}$ the density is respectively equal to 1.38 and 1.32 as presented in Table 3. These values were used to estimate the average volume occupied by each unit formed by the precursor in the materials. According to the equation

$$V_{\mathrm{a}} = [(d/\mathrm{MM})N]^{-1}$$

V_{a} is the average volume where d is the density of the hybrid xerogel, MM is the molecular weight for $-$(O$_{1.5}$-Si$-$R$-$SiO$_{1.5}$)$-$ (R = C$_2-$C$_6$H$_4-$C$_2$ and C$_6$H$_4-$C$_6$H$_4$), and N is the Avogadro number.

V_{a} was found to be equal to 274 Å^3 for $\mathbf{H_{100}}$ and 322 Å^3 for $\mathbf{H_0}$; these values are higher than the corresponding values corresponding to the volume of the unit calculated by molecular simulation using a cerius2 modelization program. By taking the distances between two oxygen atoms and assuming a cylinder shape for the unit, an average volume of 206 Å^3 for $-$(O$_{1.5}$Si$-$C$_2-$C$_6$H$_4-$C$_2-$SiO$_{1.5}$)$-$ and 198 Å^3 for $-$(O$_{1.5}$Si$-$C$_6$H$_4-$C$_6$H$_4-$SiO$_{1.5}$)$-$ was estimated. The values deduced from pycnometry indicate that organic moieties are separated from each other by important voids.

For the $\mathbf{C}_{\boldsymbol{n}}$ materials, the residue's density depends on its composition, it increased with the increase of **A**

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Table 4. Evaluation of the Porosity of Xerogels C_n

	calculated microporous volume (cm^3 g^{-1})	microporous volume (cm^3 g^{-1})	total volume (cm^3 g^{-1})	% of micro-porosity	water adsorption after 24 and 48 h (wt %)
$\mathbf{C_{80}}$	0.32	0.02	0.68	5	1.37−1.35
$\mathbf{C_{60}}$	0.20	0.30	0.59	51	1.02−1.20
$\mathbf{C_{40}}$	0.15	0.31	0.41	74	1.01−1.02
$\mathbf{C_{20}}$	0.07	0.28	0.39	71	1.60−1.65

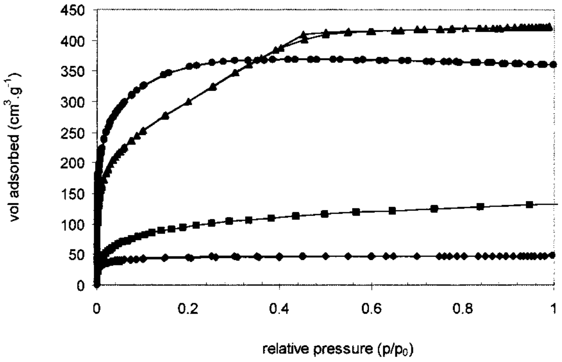

Figure 2. Adsorption−desorption isotherm plot (N_2).

in the initial $\mathbf{H}_n$ xerogel. The density for $\mathbf{C_{100}}$ was found close to the silica's density of a standard silica xerogel ($d = 2.1$),[26] while the $\mathbf{H_0}$ density is very close to that of $\mathbf{C_0}$.

N_2 and Ar Adsorption Porosimetry. N_2 and argon adsorption porosimetry allows us to evaluate the type of porosity and the materials' average pore diameters; results are presented in Tables 3 and 4. Before chemical treatment, a five-point adsorption plot measurement showed that the starting xerogels $\mathbf{H}_n$ were nonporous. After chemical treatment, all the corresponding xerogels $\mathbf{C}_n$ exhibit a high specific area around 1000 m^2 g^{-1}. However, these materials are essentially microporous and the specific area determined by BET does not have a precise meaning in these cases.

A more precise measurement of the porosity was made using a 113-point adsorption/desorption plot (Figure 2). A type I isotherm characteristic of microporous materials was obtained for all the xerogels, with a small but increasing proportion of mesopores for $\mathbf{C_{80}}$ and $\mathbf{C_{60}}$ (the volume adsorbed increases linearely until $p/p_0 = 0.4$). We note that the hysteresis loop got thicker from $\mathbf{C_{60}}$ to $\mathbf{C_{80}}$ and $\mathbf{C_{100}}$ as the ratio of **A** increases, but this phenomenon is not clearly understood at present.

Using the t-plot method (3.5 Å $< t <$ 5 Å), a low microporous volume was measured for $\mathbf{C_{80}}$ and $\mathbf{C_{100}}$ and confirms the presence of mesopores. For $\mathbf{C_{60}}$, $\mathbf{C_{40}}$, and $\mathbf{C_{20}}$, a similar microporous volume equal to 0.3 cm^3 g^{-1} is determined. The average pore size diameter was calculated using the Horvath−Kawazoe equation,[34] with a Saito−Foley cylindrical pore geometry calculation (Figure 3).[35] In all cases pore distributions become narrower when the proportion of the pillar precursor **B** in the initial xerogel is increased. For example for $\mathbf{C_{40}}$ and $\mathbf{C_{20}}$ most of the pores exhibit a diameter in the range of 10 Å, the biggest pores having a pore size between 10 and 20 Å. In contrast, for $\mathbf{C_{80}}$ and $\mathbf{C_{60}}$, most of the pore diameters are between 10 and 30 Å, but pores with a diameter between 30 and 90 Å are also present.

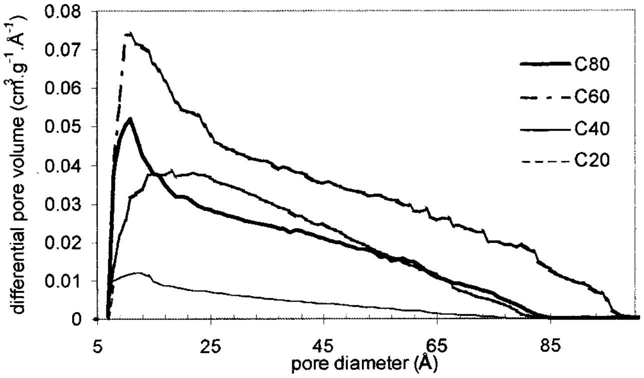

Figure 3. Horvath−Kawazoe average pore diameter plot (N_2).

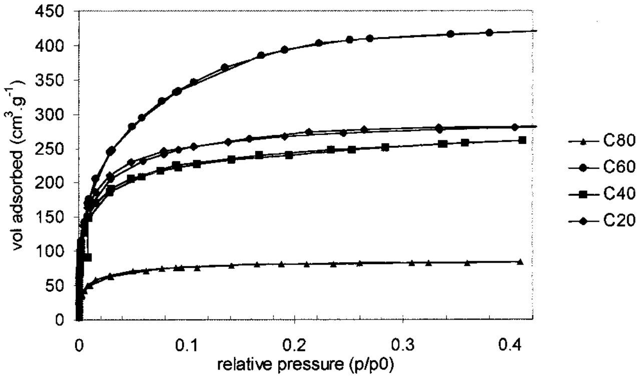

Figure 4. Adsorption desorption isotherm plot (Ar).

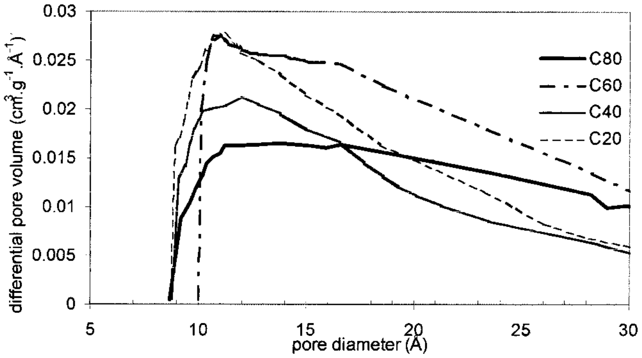

Figure 5. Horvath−Kawazoe average pore diameter plot (Ar).

Argon sorption experiments were used to evaluate mean pore diameter in the micropore region using the Horvath−Kawazoe model (Figures 4 and 5). The results are in good agreement with the N_2 sorption experiments; the micropore distributions of all the mixed hybrid xerogels increase to a maximum near 10−12 Å with a rather broad pore size distribution. The mean micropore diameters range between 5 and 30 Å, with an increasing proportion of large pores when the proportion of pillar precursor **B** is decreased. We observed some differences between the volume adsorbed of nitrogen and argon, reason for this is not clear at the present since these two gases have approximately the same molecular volumes (cross-sectional area equal to 0.162 and 0.142 nm^2 respectively). One possibility is a variation of the parameter C, which is characteristic of the interaction between the gas and the material, but

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(34) Horvath, G.; Kawazoe, K. *J. Chem. Eng. Jpn* **1983**, *16*, 470.
(35) Saito, A.; Foley, H. C. *AIChE J.* **1991**, *37*, 429.

is not precisely achievable by the BET method on microporous materials.

To explain these results we tried to estimate the volume created by the elimination of each organic group introduced by **A**. This was done by approximately assimilating the void left by the organic group into a cylindrical volume, and taking into account the formation of a Si−OH group: their presence decreases both the volume and the size of the pores. Thus, the volume created was found to be equal to 109 Å^3. It allows us to calculate a theoretical microporous volume resulting from the elimination of all the organic moieties introduced by **A**. Comparison of the theoretical values with the experimental ones indicates that microporosity is greater than calculated for $\mathbf{C_{40}}$ and $\mathbf{C_{20}}$; the opposite situation occurs for $\mathbf{C_{80}}$ (cf. Table 4). In the case of $\mathbf{C_{60}}$, the values are comparable.

Hygroscopy Measurement. The amount of water adsorbed at 25 °C in a 60% humidity atmosphere was determined after 24 and 48 h (Table 4). This measurement allows a qualitative description of the presence of silanol functions on the surface of a silica. For the xerogels $\mathbf{C}_{\boldsymbol{n}}$, the quantity of adsorbed water is always very low (<2%) despite their high surface area (> 800 m^2 g^{-1}). In comparison, a water adsorption of 20 to 40 wt % is usually expected for silica xerogel with such high surface area. The low affinity of $\mathbf{C}_{\boldsymbol{n}}$ for water can be caused by the presence of the hydrophobic biphenyl groups and the hydrophobic siloxane linkages.

Discussion

The present system was developed in order to investigate the possibility of generating porosity in an hybrid organic−inorganic xerogel. This was attempted by removing a selected organic group from a hybrid xerogel made of two precursors with similar features (size and rigidity). The organic group introduced by one of the precursors serves as a template to generate the porosity, the organic group introduced by the other one serving as a pillar. For the present system, three questions arise: on the proportion and the distribution of the precursors in the initial xerogels, on the effect of the chemical treatment, and on the porosity origin and characteristics of the resulting material.

Proportion and Distribution of the Precursors in the Initial Xerogels. The hybrid organic−inorganic xerogel was prepared by copolycondensation of two precursors, one of them containing the removable organic group. For this polymerization step, a reactivity higher for **A** than for **B** was found, using HCl as catalyst decreases this difference of reactivity. It also appears that **A** can act as a catalyst of the gelation of **B** since gelation times of the mixtures were all close to **A**'s gelation time, even when low proportions of this precursor were used. The different data confirm the complete copolycondensation of the two precursors, but questions remain on the copolycondensation process, which can schematically occur by a random or a segregative process. In the last case a selective polycondensation of **A** on itself is followed by the polycondensation of **B**; in the first case a random polycondensation of **A** and **B** occurs and is only dependent on the molar ratio of the precursor. Part of the answer is given by the porosity of the materials after chemical treatment.

Effect of the Chemical Treatment. The treatment of $\mathbf{H}_{\boldsymbol{n}}$ with a mixture of an excess of methanol and water in the presence of fluoride catalyst (NH_4F) efficiently and selectively removed all the organic group introduced by **A** without elimination of the group introduced by **B**. The NMR data demonstrate the elimination of the C_{sp} carbon atoms and the formation of Q^n units. Indeed, the corresponding 1,4-bis(ethynyl)benzene is recovered quantitatively with no formation of biphenyl. This F^--catalyzed hydrolysis of a Si−C_{sp} bond is a well-documented process in organosilicon chemistry.[36−38] This chemical treatment is performed in all cases on a nonporous material, and we assume that pores are formed at first on the surface of the material providing an access for the reagent to the reactive center inside the material. Meanwhile, the hydrolysis of the Si−C_{sp} bonds leads to Si−OH, and their polycondensation with Si−OR (R = H and Me) occurs as demonstrated by the NMR data. This process leads to an increase of the material's condensation level and a coarsening of the silica network. In addition, previous studies have demonstrated that this chemical treatment using a F^- catalyst may produce a reorganization of the silica network that would limit the possibility to precisely design the porosity.[21,22,30]

Porosity: Origin and Characteristics. The high specific surface area of the $\mathbf{C}_{\boldsymbol{n}}$ is related to the elimination of the organic spacer and depends greatly on the composition of the corresponding $\mathbf{H}_{\boldsymbol{n}}$.

When high percentages of **B** are used, $\mathbf{C_{20}}$ and $\mathbf{C_{40}}$, purely microporous materials are obtained, the mean pore size being around 5−20 Å, close to the size of the removed organic group (11.5 Å). Pores smaller than 11.5 Å may result from the formation of the Si−OH groups, which undergo a polycondensation. Pores bigger than 11.5 Å may result from the association of two to three units of **A** in $\mathbf{H}_{\boldsymbol{n}}$ and also from the voids that initially separate the organic units and are now added to the void left by the chemical treatment. These results agree with a random copolycondensation and a homogeneous distribution of the two precursors as depicted in Scheme 3b. The opposite situation, a segregative copolycondensation, should lead to the formation of large pores as shown in Scheme 3a.

When low percentages of **B** are used, $\mathbf{C_{60}}$ and $\mathbf{C_{80}}$, the material exhibits essentially micropores (<20 Å) but also mesopores (20−100 Å). The presence of a high amount of precursor **A** at the polycondensation step leads necessarily to the proximity of removable organic groups. Consequently, mesopores are formed by the elimination of some organic spacers packed together and by the percolation of the voids left by each organic group. The chemical treatment leads to a rather extended silica network with an average of 2.5 to 5 SiO_2 units for one biphenyl pillar.

Finally, in all cases, the size discrepancy between the pore and the removed organic spacer may also result from a F^--induced evolution of the silica network: a redistribution reaction of the Si−O bonds occurring in

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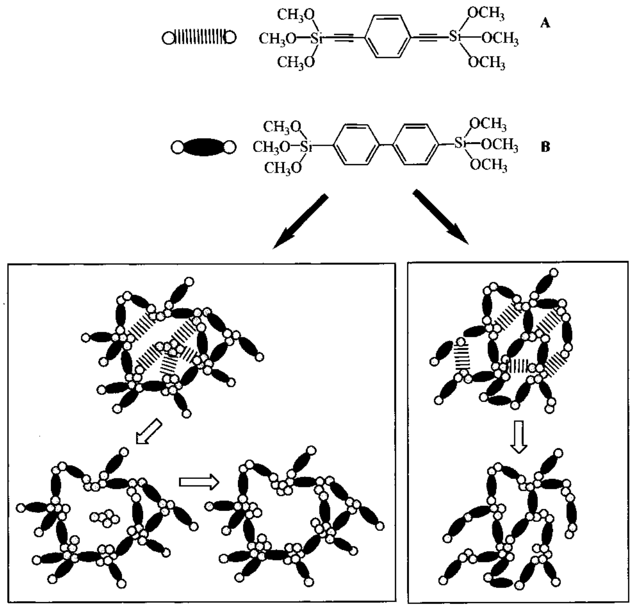
(36) Kuwajima, I.; Nakamura, E.; Hashimoto, K. *Tetrahedron* **1983**, *39*, 975.

(37) Chuit, C.; Corriu, R. J. P.; Reyé, C. *J. Organomet. Chem.* **1988**, *358*, 57.

(38) Chuit, C.; Corriu, R. J. P.; Reyé, C.; Young, C. *Chem. Rev.* **1993**, *93*, 1371.

Scheme 3



Scheme 3a Scheme 3b

the solid competitively to a polycondensation of the Si−OR (R = H or Me) functions.[18,22,30]

Conclusion

Porosity in a silica-based hybrid organic−inorganic xerogel was created by chemical treatment of an hybrid xerogel of general formula $\{[(O)_{1.5}Si{-}C{\equiv}C{-}R{-}C{\equiv}C{-}Si(O)_{1.5}]_x[(O)_{1.5}Si{-}R'{-}Si(O)_{1.5}]_{1-x}\}$. The complete and selective elimination of C≡C−R−C≡C was achieved while the nonremovable R′ groups serve as pillars. The size and the proportion of the pores created by chemical treatment is the sum of three main parameters: the size of R, its proportion and the distribution of R and R′ groups in the material. A high level of microporosity can be achieved with a high proportion of pillars while decreasing this proportion leads to the formation of a mesoporosity.

Experimental Section

^{29}Si NMR and ^{13}C solid-state NMR spectra were obtained on a Bruker AM300 instrument at 59.620 MHz for ^{29}Si spectra and 75.469 MHz for ^{13}C spectra. Contact time was 2000 μs, with 1389 scans, 10 s of recycle time, and a spinning rate of 5 MHz. Elemental analyses were performed by “Service Central de Microanalyse du CNRS”. Surface area measurements were conducted on Micromeritics Gemini and ASAP 2010 porosimeters using high purity N_2 or Ar as adsorbate at −196 °C. Surface areas were calculated by the BET equation, micropore volumes calculated using a *t*-plot, and pore size distribution calculated using the Horvath−Kawazoe equation with Saito−Foley cylindrical pore geometry. Helium pycnometry measurements were performed on a Accupyc1330 pycnometer. Samples were dried under vacuum at 100 °C for 12 h. Water adsorption measurements were performed on dried sample. Commercial solvents (Aldrich) were purified and dried by standard methods according to previous literature.[39] All manipulations were performed under nitrogen using Schlenkware and a vacuum/nitrogen line.

Preparation of 1,4-Bis(trimethoxysilylethynyl)benzene (A). This precursor was synthesized as described by Chevalier et al.[22]

Preparation of 4,4′-Bis(trimethoxysilyl)biphenyl (B). This precursor was synthesized using an experimental procedure similar to the one described by Shea et al.[16] In a 500 mL round-bottom flask equipped with a reflux condenser were placed a mixture of magnesium turnings (6.45 g, 265 mmol), trimethoxychlorosilane (79.69 g, 509 mmol), and THF (50 mL). A solution of 4,4′-dibromobiphenyl (31.95 g, 102 mmol) in THF (150 mL) was added dropwise (1.5 h). The mixture was kept at reflux (75 °C) for 24 h. Excess magnesium and salts were separated by filtration and washed with pentane (3 × 100 mL). Solvent was evaporated off, and the resulting oily residue was distilled. Distillation (5×10^{-2} mmHg, 175 °C) gave 14.12 g of a yellowish oil that solidifies slowly at room temperature; yield 35.5%. ^{1}H NMR ($CDCl_3$, δ): 3.66 (s, 17H); 7.67 (d, 4H); 7,74 (d, 4H). ^{13}C NMR ($CDCl_3$, δ): 51.1, 127.0, 128.7, 135.5, 143.2. ^{29}Si NMR ($CDCl_3$, δ): −56.1.

General Procedure for the Synthesis of the Xerogels. In a Schlenk flask under nitrogen, precursors **A** and/or **B** and THF were mixed and stirred vigorously. The reagents H_2O (13 M in THF solution) and HCl (1 M in diethyl ether solution) were added, and the whole clear and homogeneous solution was stirred for an additional 2 min. The stirring was then stopped and gelation occured, forming at first a gel that occupies the same volume as the initial solution. The gel was allowed to to stand to age for 1 week, and the resulting solid was then crushed, washed three times with ethyl ether (50 mL), and dried for 24 h at 100 °C under vacuum (0.1 mmHg). The same experimental procedure was used for the preparation of all the xerogels.

Xerogel $\mathbf{H}_{100}$. Mixture for gelation was made with 0.9 g, (2.5 mmol) of **A**, 2.5×10^{-2} mmol of HCl, 7.6 mmol of water, and 2.5 mL of THF. Gelation time was 10 min. Mass of xerogel: 0.65 g. Yield: 115%. Anal. Found: C, 50.13; H, 3.98; Si, 22.5. ^{29}Si NMR CP−MAS (δ): −77.4 (T_A^1); −87.0 (T_A^2); −93.8 (T_A^3). ^{13}C NMR CP−MAS (δ): 132.3; 123.1; 102.5; 89.9; 50.6.

Xerogel $\mathbf{H}_{80}$. Mixture for gelation was made with 4.62 g, (12.6 mmol) of **A**, 1.21 g (3.1 mmol) of **B**, 15.9×10^{-2} mmol of HCl, 47.1 mmol of water, and 16 mL of THF. Gelation time was 75 min. Yield 110%. Mass of xerogel: 4.04 g. Anal. Found: C, 53.41; H, 2.05; Si, 24.01. ^{29}Si NMR CP−MAS (δ): −59.0 (T_B^1); −67.7 (T_B^2); −78.2 (T_B^3+T_A^1); −87.4 (T_A^2); −96.2 (T_A^3). ^{13}C NMR CP−MAS (δ): 142.2; 135.6; 132.3; 127.0; 122.6; 103.3; 88.5; 56.2; 50.7.

Xerogel $\mathbf{H}_{60}$. Mixture for gelation was made with 3.27 g, (8.9 mmol) of **A**, 2.35 g (6.0 mmol) of **B**, 14.8×10^{-2} mmol of HCl, 44.7 mmol of water, and 14 mL of THF. Gelation time was 75 min. Mass of xerogel: 3.87 g. Yield: 109%. Anal. Found: C, 54.16; H, 2.34; Si, 23.45. ^{29}Si NMR CP−MAS (δ): −60.8 (T_B^1); −68.3 (T_B^2); −77.8 (T_B^3+T_A^1); −87.0 (T_A^2); −95.7 (T_A^3). ^{13}C NMR CP−MAS (δ): 142.2; 135.6, 132.2; 126.5; 122.6; 103.1; 88.7; 56.1; 49.9.

Xerogel $\mathbf{H}_{40}$. Mixture for gelation was made with 2.44 g, (6.6 mmol) of **A**, 4.05 g (10.3 mmol) of **B**, 16.8×10^{-2} mmol of HCl, 5.7 mmol of water, and 12 mL of THF. Gelation time was 55 min. Mass of xerogel: 4.61 g. Yield: 111%. Anal. Found: C, 54.89; H, 2.61; Si, 22.92. ^{29}Si NMR CP−MAS (δ): −60.9 (T_B^1); −68.4 (T_B^2); −77.7 (T_B^3+T_A^1); −87.1 (T_A^2); −94.0(T_A^3). ^{13}C NMR CP−MAS (δ): 142.4; 135.2; 132.0; 126.5; 122.6; 102.9; 88.6; 56.4; 49.7.

Xerogel $\mathbf{H}_{20}$. Mixture for gelation was made with 0.93 g, (2.5 mmol) of **A**, 4.22 g (10.7 mmol) of **B**, 13.2×10^{-2} mmol of HCl, 39.6 mmol of water, and 10 mL of THF. Gelation time was 45 min. Mass of xerogel: 4.64 g. Yield: 109%. Anal. Found: C, 55.60; H, 2.87; Si, 24.41. ^{29}Si NMR CP−MAS (δ): −59.8 (T_B^1); −68.2 (T_B^2); −77.1 (T_B^3+T_A^1); −87.6 (T_A^2); −93.10 (T_A^3). ^{13}C NMR CP−MAS (δ): 142.4; 135.3; 131.8; 126.7; 122.8; 102.2; 89.5; 61.6; 50.5.

Xerogel $\mathbf{H}_{0}$. Mixture for gelation was made with 1.64 g (4.2 mmol) of **B**, 4.1×10^{-2} mmol of HCl, 12.6 mmol of water and 4.16 mL of THF. Gelation time was 600 min. Mass of xerogel: 1.08 g. Yield: 102%. Anal. Found: C, 51.63; H, 3.88; Si, 19.5. ^{29}Si NMR CP−MAS (δ): −59.8 (T_B^1); −68.2 (T_B^2); −77.1 (T_B^3) ^{13}C NMR CP−MAS (δ):142.2; 135.3; 128.9; 60.6.

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General Procedure for the Chemical Treatment. Chemical treatment of all the xerogels $\mathbf{H}_n$ ($n = 100, 80, 60, 40, 20, 0$) was performed with the same experimental procedure. The xerogel was introduced into a 250 mL round-bottom flask equipped with a reflux condenser. The solution of water, methanol, and NH_4F was added and the heterogeneous mixture heated at 60 °C without stirring under nitrogen. After 4 days the product was filtered and the remaining solid was washed with H_2O (10 mL), THF (20 mL, 3 times), acetone (20 mL, 3 times), and ethyl ether (20 mL). The residual solid was then dried for 24 h at room temperature under vacuum (1 mmHg). The filtrates were combined and the solvents were evaporated, giving a solid residue characterized as 1,4-bis(ethynyl)benzene.

Treatment of $\mathbf{H}_{100}$. Mass of $\mathbf{H}_{100}$: 9.54 g. Mass of $\mathbf{C}_{100}$: 4.85 g. Anal. Found: C, 5.77; H, 1.71; Si, 38.62. ^{29}Si NMR CP−MAS (δ): −90.4 (Q_A^2); −100.2 (Q_A^3); −109.7 (Q_A^4). ^{13}C NMR CP−MAS δ: no signals. Mass of bis(1,4-ethynyl)benzene: 4.53 g.

Treatment of $\mathbf{H}_{80}$. Mass of $\mathbf{H}_{80}$: 2.73 g. Mass of $\mathbf{C}_{80}$: 1.58 g. Anal. Found: C, 19.35; H, 2.15; Si, 37.70. ^{29}Si NMR CP−MAS (δ): −68.7 (T_B^2); −76.9 (T_B^3); −90.4 (Q_A^2); −100.2 (Q_A^3); −109.7 (Q_A^4). ^{13}C NMR CP−MAS (δ): 143.2; 134.3; 128.8; 125.9; 60.8. Mass of 1,4-diethynylbenzene: 1.58 g.

Treatment of $\mathbf{H}_{60}$. Mass of $\mathbf{H}_{60}$: 2.71 g. Mass of $\mathbf{C}_{60}$: 1.79 g. Anal. Found: C, 32.79; H, 2.50; Si, 31.94. ^{29}Si NMR CP−MAS (δ): −59.7 (T_B^1); −68.7 (T_B^2); −77.5 (T_B^3); −90.3 (Q_A^2); −99.6 (Q_A^3); −108.5 (Q_A^4). ^{13}C NMR CP−MAS (δ): 142.8; 134.5; 129.5; 125.0; 59.7. Mass of 1,4-diethynylbenzene: 0.76 g.

Treatment of $\mathbf{H}_{40}$. Mass of $\mathbf{H}_{40}$: 3.01 g. Mass of $\mathbf{C}_{40}$: 2.29 g. Anal. Found: C, 42.67; H, 2.76, Si, 27.71. ^{29}Si NMR CP−MAS (δ): −60.5 (T_B^1); −69.3 (T_B^2); −77.9 (T_B^3); −90.9 (Q_A^2); −99.8 (Q_A^3); −107.2 (Q_A^4). ^{13}C NMR CP−MAS (δ): 142.7; 135.0; 128.8; 128.6. Mass of 1,4-diethynylbenzene: 0.47 g.

Treatment of $\mathbf{H}_{20}$. Mass of $\mathbf{H}_{20}$: 2.53 g. Mass of $\mathbf{C}_{20}$: 2.21 g. Anal. Found: C, 51.65; H, 2.90; Si, 23.97. ^{29}Si NMR CP−MAS (δ): −59.6 (T_B^1); −68.8 (T_B^2); −76.7 (T_B^3); −90.4 (Q_A^2); −98.8 (Q_A^3); −106.7 (Q_A^4). ^{13}C NMR CP−MAS (δ):142.5; 134.7; 126.2. Mass of 1,4-diethynylbenzene: 0.68 g.

Treatment of $\mathbf{H}_{0}$. Mass of $\mathbf{H}_{0}$: 5.02 g. Mass of $\mathbf{C}_{0}$: 4.85 g. Anal. Found: C, 53.38; H, 3.60; Si, 20.66. ^{29}Si NMR CP−MAS (δ): −59.6 (T_B^1); −68.8 (T_B^2); −76.7 (T_B^3). ^{13}C NMR CP−MAS δ:142.3; 131.8; 126.9.

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