Hybrid Silica Gels Containing 1,3-Butadiyne Bridging Units. Thermal and Chemical Reactivity of the Organic Fragment

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Silica gel containing diyne units have been obtained from molecular organosilicon precursors and the properties associated to the very reactive unsaturated organic moieties have been explored. The sol–gel polymerization of 1,4-bis(trimethoxysilyl)-1,3-butadiyne ($(MeO)_3SiC \equiv CC \equiv CSi(OMe)_3$) quantitatively led to a silsesquioxane network, $[O_{1.5}$-$SiC \equiv CC \equiv CSiO_{1.5}]_n$, consisting of siloxanes chains with bridging diyne units. The derived xerogels were characterized by IR and ^{13}C and ^{29}Si CP MAS NMR spectroscopies. The major environment of the Si atom corresponded to a T^2 C*Si*(OR)(OSi)$_2$ substructure, and only minor Si–C bond cleavage occurred during the sol–gel condensation. The chemical reactivity of the hybrid organic–inorganic gel was studied and used as a tool for the study of the organization of the solid induced by the organic moieties. Upon heating, in the solid state, the diyne fragments undergo a polyaddition to give an ene–yne structure. The polymerization, observed in the solid state, suggests favorable arrangements of the organic fragments within the amorphous solid. The resulting composite material consists in a network made of interpenetrating ene–yne and siloxane polymers. On the other hand, the organic diyne fragments in the hybrid gel have been removed, leaving silica behind, in two ways: (i) The thermal oxidation in air led to microporous silicas with N_2 BET surface areas in the range $300-350$ m^2 g^{-1}. (ii) Interestingly, the smooth Si–C bond cleavage by MeOH catalyzed by NH_4F gave highly porous silica with N_2 BET surface areas up to 950 m^2 g^{-1}. The latter elimination of the organic moiety under mild reaction conditions is of particular interest since it gives rise to silica with a surface area significantly higher than that produced upon thermal oxidation and higher than that of the originating hybrid precursor.

Introduction

The sol–gel process, which offered unique possibilities for the elaboration of inorganic solids,[1] also recently proved to be of great interest for the preparation of hybrid organic–inorganic materials. The hydrolysis and polycondensation of substituted alkoxysilanes RSi-(OR′)$_3$ containing a nonhydrolyzable Si–C bond gave rise to a variety of silsesquioxanes[2] (eq 1). Materials with unique properties and applications can be produced upon changing the nature of the organic substituent.

$$n\mathrm{RSi(OR')}_3 \xrightarrow[\;-\mathrm{R'OH}\;]{\mathrm{H_2O}} [\mathrm{RSiO_{1.5}}]_n \quad (1)$$
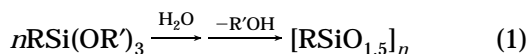
Di- or polysilylated organic molecules were shown to give an easy versatile access to amorphous microporous

hybrid materials (eq 2). In an approach to control the morphology of the resulting solid at the molecular level, organic fragments with various structural features were introduced.[3,4]

$$n\mathrm{(RO)_3SiXSi(OR)_3} \xrightarrow{\mathrm{H_2O}} [\mathrm{O_{1.5}SiXSiO_{1.5}}]_n \quad (2)$$
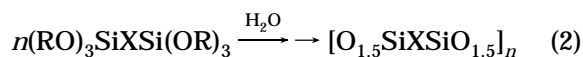
This can be also used for inserting functional organic group in a silicate network to produce hybrid gels with interesting reactivity. Silica gels with electroactive properties were for example obtained from molecular precursors containing thiophene oligomers.[5]

We decided to investigate the properties of gels containing diacetylene units: $(O_{1.5}SiC \equiv CC \equiv CSiO_{1.5})$. Such molecularly defined hybrid silicate diyne network should be prepared easily from organosilicon precursor. Moreover the solid material should exhibit a high reactivity in two ways:

(i) Polymerization of the highly reactive diyne fragment: diacetylene molecules are known to polymerize

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⊗ Abstract published in *Advance ACS Abstracts,* November 1, 1995.
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in the solid state upon thermolysis or photolysis[6−8] (eq 3).
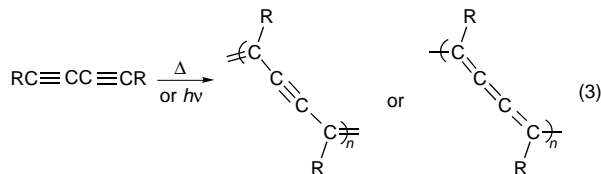
Such a polymerization within an inorganic silicate network may lead to new composite materials consisting of interpenetrating organic and inorganic polymer chains.

(ii) Cleavage reaction of the Si−C bond: Ethynyl silanes readily undergo nucleophilic substitution reactions at silicon.[9] The elimination of the organic moieties from the hybrid gel under smooth reaction conditions may lead to inorganic solids with high porosity. The control of pore size of silica, based on organic−inorganic hybrid, is of particular interest. Several groups recently reported the use of sacrificial organic template molecules. Porous silicas were obtained by means of pyrolysis of organic−inorganic hybrid.[10−13]

Therefore it seemed that the reactions of silica gels containing reactive diacetylene chain unit could generate new material and change certain morphological properties of the material. We wish to report here our studies on the reactivity of diacetylene bridged silsesquioxanes and to show its potential for "controlled" alteration of the microstructure of the resulting material.

Results and Discussion

Preparation of Diyne-Bridged Silsesquioxane Gels. The silsesquioxane gels containing 1,3-butadiyne units were obtained upon sol−gel polymerization of 1,4-bis(trimethoxysilyl)-1,3-butadiyne **1** (eq 4). Methanolic solutions of the diacetylene derivative **1**, prepared by silylation of 1,4-dilithio-1,3-butadiyne with ClSi(OMe)$_3$,[14] were hydrolyzed in the presence of fluoride ion as catalyst.[15] The hydrolysis polycondensation was performed under reaction conditions similar to those used for related precursors.[4]
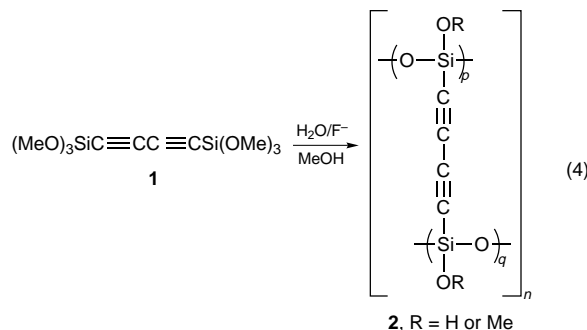
Transparent gels formed within a short period of time, 5 min to 3 h depending on the concentration of the precursor in the solution (0.3−3 mol L^{-1}). After standing for ca. 7 days, the gels were powdered, washed with ether, and dried in vacuo. The resulting solids were analyzed and characterized by IR and solid-state ^{13}C and ^{29}Si NMR spectroscopies. The obtained materials presented similar characteristics and only those of the gel **2**, resulting from the hydrolysis and polycondensation of 1 M methanolic solution of **1**, will be discussed below. The gel **2** deviated from the silsesquioxane stoichiometry, $[O_{1.5}SiC_4SiO_{1.5}]_n$. The analysis revealed an elemental composition $[SiC_{2.02}O_{2.3}H_{1.1}]$ with an excess of oxygen, which is indicative of the presence of uncondensed Si−OH groups in the material. The FT-IR spectrum also indicated the presence of residual hydroxy groups together with some methoxy groups (ν(C−H) 2845 cm^{-1}). The most interesting features arose from the examination of the ν(C≡C) region. Beside the vibration centered at 2091 cm^{-1}, assigned to the diyne bridging unit (SiC≡CC≡CSi) the spectrum exhibited low intensity absorption at 2045 and 2202 cm^{-1}. These were attributed to vibration of C≡C bonds in SiC≡CC≡CH units. The presence of a terminal acetylene group was confirmed by the presence of a weak absorption at 3295 cm^{-1}. It thus appeared that little cleavage of the Si−C bond had occurred during the sol−gel polymerization of **1**, since the Si−C bond is labile to some extent in methanol in the presence of fluoride ion catalyst.[9] However the hydrolysis polycondensation, performed at room temperature, did not cause much cleavage of Si−C bonds. The CP MAS NMR studies showed that the structure of the organometallic precursor was essentially retained within the solid. The ^{13}C and ^{29}Si NMR spectra gave no evidence for Si−C bond breaking. The ^{13}C resonances of the two kind of acetylenic carbons in SiC≡CC≡CSi were observed at −80.7 and −87.8 ppm. The ^{29}Si NMR spectrum showed three resonances at −80.7, −89.9, and −99.5 ppm in agreement with C*Si*O$_3$ substructures. The major resonance at −89.9 ppm, corresponding to substructure T^2

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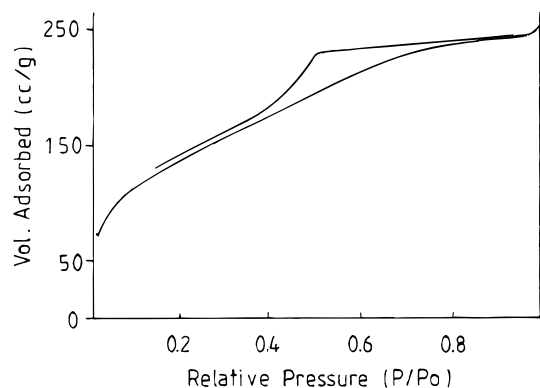
Figure 1. N$_2$ adsorption–desorption isotherm of **2**.

Table 1. Surface Area,[a] Pore Volume, and Mean Pore Diameter Data

entry	amorphous material	surface area ($m^2 \cdot g^{-1}$)	pore vol ($mL\ g^{-1}$)	mean pore diam (Å)
a	**2**	467	0.38	32.0
b	**3**	216	0.20	37.0
c	**4**	348	0.23	26.0
d	**5**	333	0.22	26.8
e	**6**	302	0.23	30.3
f	**7**	905	0.66	29.0
g	**8**	950	0.68	28.7
h	**9**	800	0.56	28.1

[a] BET surface determined with nitrogen.[17]

$\equiv$ CSi(OR)(OSi$\equiv$)$_2$ is consistent with the mean structure **2** presented in eq 1. Similar degrees of condensation were previously observed for related materials.[4] No signal at −110 ppm, attributable to SiO$_4$ substructures,[16] which would be produced by Si−C bond cleavage, was found. Therefore, the presence of some SiC$\equiv$CC$\equiv$CH units, as indicated by the IR spectroscopy, is due to the high sensitivity of the spectroscopy and corresponds to minor bond cleavage during the sol−gel condensation.

The xerogel **2** was a porous amorphous material. The X-ray powder diffraction pattern showed two broad bands with *d* spacings of 3.9 and 8.1 Å and no crystallinity. N$_2$ BET[17] measurement revealed a surface area of 467 m^2 g^{-1}. The N$_2$ adsorption−desorption isotherm (Figure 1) exhibited hystereses and indicated a substantial microporosity. The mean pore diameter was 32 Å (cf. Table 1, entry a). The distribution rises to a maximum at 39 Å.

Polymerization of the Bridging Diyne Units. Pyrolysis of Gel 2 under Argon

Upon thermolysis, organosilicon polymers containing diyne units have been shown to cross-link through a polyaddition of the acetylenic units.[7,8] The thermal reactivity was correlated to the crystallinity of the polymeric material and the distance between the reactive chain units.[7c] We thus explored the thermal reactivity of the gel **2** containing diyne groups. While amorphous, the mixed silica framework **2** may allow a reaction between proximal diyne fragments to give a more cross-linked material.

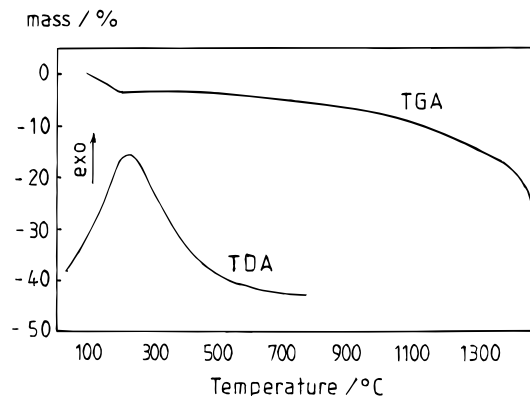We first examined the thermogravimetric and thermal differential analyses under an inert gas. The

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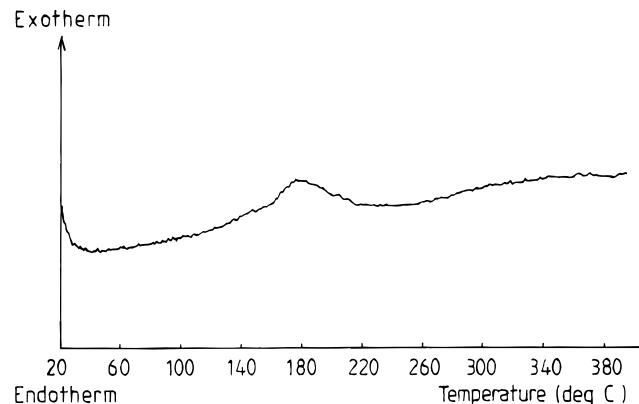**Figure 2.** TGA and TDA curves of **2**.

Figure 3. DSC curve of **2**.

thermogram is shown in Figure 2. The TGA trace revealed that different steps take place successively when the temperature increased up to 1200 °C. After an initial weight loss (ca. 4%) below 200 °C, it was stable up to 500 °C. At this point, decomposition started to give a progressive weight loss and a low yield of residue. The TDA curve showed a strong exotherm in the temperature range 200−400 °C, with a maximum at 230 °C. The observed initial weight loss (below 200 °C) is due to the elimination of adsorbed solvent of the partially dried material **2**. Owing to their low thermal stability, the hybrid gels containing the diyne fragments were dried only in vacuo at 20 °C. Mass spectrometric analysis of the gas evolved at the initial stage of heating, for example, revealed the presence of diethyl ether which was not completely eliminated from gel **2** at room temperature. In a second step, reaction of diyne units occurred. The analysis of the differential scanning calorimetry (DSC) curve revealed main features which are consistent with the above data. As shown in Figure 3 an exotherm centered at 175 °C and corresponding to ΔH ca. 135 cal g^{-1} was observed. The exotherm is consistent with a cross-polymerization of diyne units. This behavior was previously observed in the thermolysis of linear poly[(silylene)diacetylenes][7] and more recently with siloxane−diacetylene polymers.[8] The thermolysis first caused a rearrangement of the diacetylene fragment to a more stable structure. Then at high temperature, decomposition of the mixed-oxide material probably occurred. The carboreduction of pyrolyzed poly[(silylene)diacetylenes] metal oxide composites was previously described.[18]

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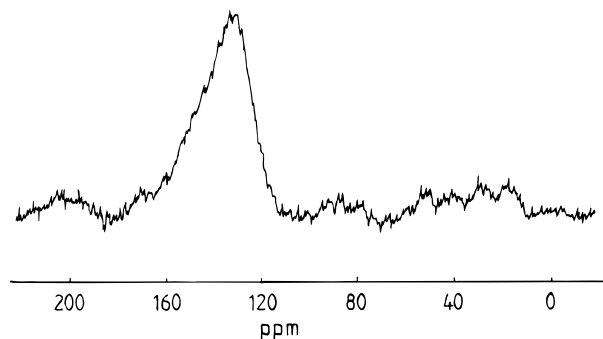**Figure 4.** ^{13}C CP MAS NMR of **3**.

The polymerization of diacetylene units according to eq 3, with formation of ene-yne structures is a well established process.[6,7] The cross-linking in poly[(silylene) diacetylene] was shown to occur at temperature ranging from 200 to 315 °C depending on the environment of the diacetylene groups. The lowest cross-linking temperature was found for the most crystalline polymer with short interchain distances.[7c] In the case of the amorphous hybrid gel **2**, the polymerization can occur via polyaddition of the acetylene units according to eq 5.

(5)

2, R = H or Me
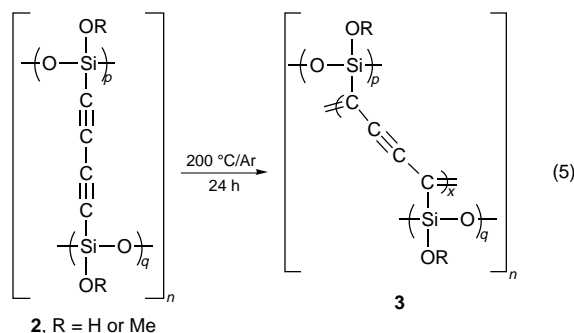
The proposed thermal reactions is supported by the analysis of pyrolyzed samples of hybrid gel **2**. The gel **2** was pyrolyzed at 200 °C for 24 h. in an inert atmosphere. The resulting new solid **3** analyzed as $SiC_{2.1}O_{2.05}H_{1.5}$ consistently with the reaction in eq 5. The FTIR spectrum revealed an additional new band at 2169 cm^{-1} which can be assigned to the vibration of the C≡C bond in the ene−yne structure.[6,7] Additional characterization came from the examination of **3** by solid state NMR. The ^{13}C MAS NMR spectrum (cf. Figure 4) showed only a broad signal centered at 133 ppm. The latter, in agreement with a polymerization of the acetylenic unit, can be attributed to resonances of sp^2 carbon atoms. The ^{29}Si CP MAS NMR also revealed a broad resonance centered at −74 ppm in the characteristic region of C sp^2 SiO_3 substructures. However intense resonances at −91.0, −100.2, and −110.1 ppm also appeared (Figure 5). The resonance at −110 ppm resulting from the presence of a Q^4 substructure Si(O-Si)$_4$ unambiguously indicated that partial Si−C bond breaking had occurred during the thermolysis. The extent of the Si−C bond cleavage is difficult to establish, since the signals arising from C sp SiO_3 (T^2, T^3) and those arising from $SiO4$ (Q^2, Q^3) substructures overlap[4] in the region −90 to −100 ppm.

Some solid-state properties of **3**, consisting of a mixed silicate network and an ene−yne organic polymer, are given in Table 1. The N$_2$ BET surface area (216 m^2 g^{-1}) and pore volume (0.2 mL g^{-1}) in **3** are significantly lower
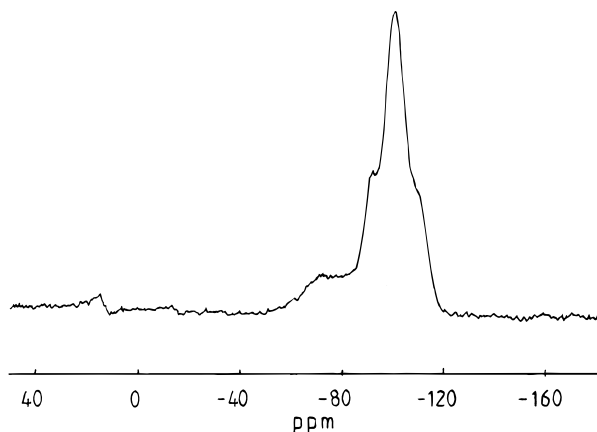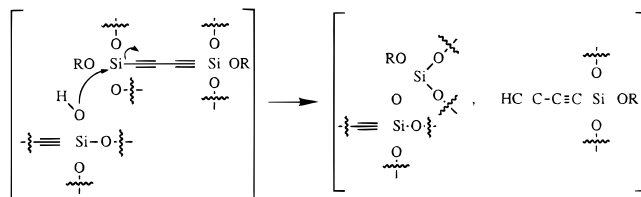

Figure 5. ^{29}Si CP MAS NMR of **3**.

Scheme 1 Nucleophilic Cleavage of Si−C Bond in Gel 2

than the values measured for **2**. The polymerization of the acetylenic moieties, resulting in extensive cross-linking in **3**, is probably responsible for the reduced porosity and surface area of the material.

The cleavage of the Si−C bond which occurred to some extent upon heating gel **2** probably arises from a nucleophilic reaction of residual uncondensed hydroxy groups.[9] As shown in Scheme 1, the reaction of a proximal uncondensed Si−OH group led to a SiO$_4$ unit. This is accompanied by the formation of a terminal acetylene unit O$_3$SiC≡CC≡CH. The latter rapidly polymerized to ene−yne. Therefore the observed polyaddition of the diyne units in gel **2** probably arises both from the reaction of disilylated SiC≡CC≡CSi and monosilylated SiC≡CC≡CH diyne units.

As noted earlier, in the case of gel **2**, the polymerization of the diyne unit occurred at a relatively low temperature. The associated exotherm peak appeared at temperatures ranging from 175 to 200 °C. Short distances between the SiC≡CC≡CSi units within the amorphous material might account for this behavior. This was demonstrated in the case of other diyne polymers.[7c] However, in the present case, the significant broadening of the exothermic area contrasts with the sharp exotherm peak observed for crystalline materials.[7] The broadening may be indicative of a more complex process here. Although it may be associated to slow reaction, it is most probably related to the existence of different arrangements and orientations of the neighboring diyne fragments in the amorphous material.

From the above results we can conclude that the pyrolysis of the gel **2**, with bridging diacetylene units, caused the polymerization of the diyne group to yield a more cross-linked hybrid organic−inorganic network **3**. The thermal reaction which occurred at a relatively low temperature indicates that the diyne units are closed to each other in the amorphous solid. However this thermal reaction is associated to some Si−C bond cleavage inducing a partial reorganization of the silicate
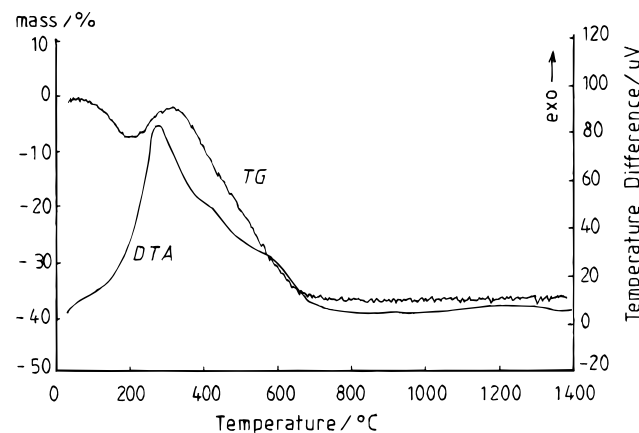
Figure 6. TGA and TDA curves of **2** (O_2 flow).

framework. It also produces highly reactive terminal diyne units which contribute to the formation of the ene—yne chain in the solid.

Preparation of Silica-Based Materials from Hybrid Diynylene-Bridged Silsesquioxanes

Hybrid silica gels have been used as silica precursors in attempt to obtain materials with controlled porosity.[10-13] We also studied the possible elimination of the organic moiety in the hybrid diyne material to generate a purely inorganic solid. We envisaged the cleavage of the Si—C bond by oxidation at high temperature and by nucleophilic substitution at silicon under smooth reaction conditions. To evaluate the consequences on the microstructure of the resulting silica material, we examined some of its solid-state properties.

Pyrolysis of Hybrid Gels 2 and 3 in Air. The observed high reactivity of the diyne fragments led us to examine the thermolysis of **2** under a flow of O_2. We first carried out the thermogravimetric analysis of the gel **2** containing diyne bridging units. A sample of **2** was heated in air at a rate of 10 °C min^{-1} between 20 and 1400 °C. The thermogram is presented in Figure 6 and showed several steps. The first weight loss (ca. 7%) between 20 and 200 °C is due, as mentioned earlier, to the elimination of adsorbed solvent molecules. Then, a weight uptake of ca. 5%, between 200 and 300 °C is indicative of an oxidation step. The oxidation of Si—C probably started at those temperatures. Above 300 °C, the calcination of the organic moiety resulted in a 34% weight loss closed to the theoretical value (ca. 31%). Complete elimination of carbon is achieved at 650 °C as indicated by a weight of residue which remained unchanged up to 1400 °C.

To characterize the inorganic residue, the pyrolysis was achieved on a preparative scale. The gel **2** was first heated at 400 °C under an O_2 flow for 4 h (eq 6). The
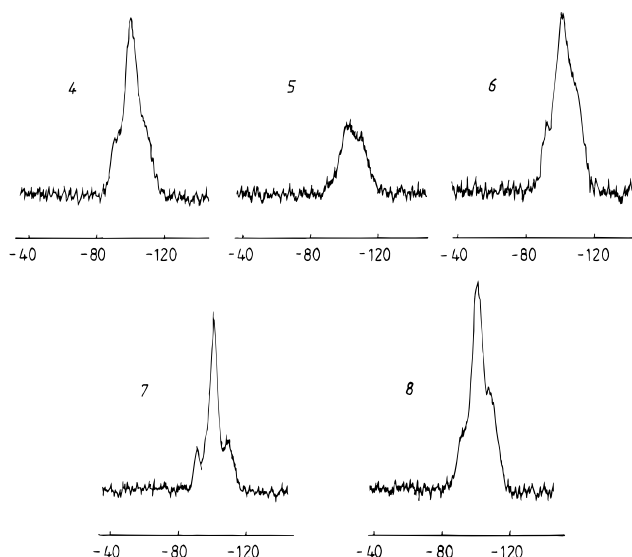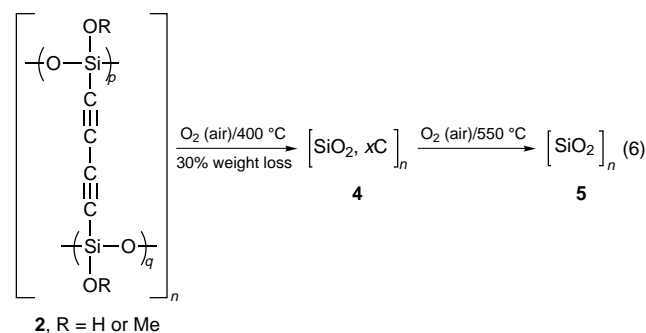

2, R = H or Me

Figure 7. ^{29}Si CP MAS NMR spectra of silica materials **4**—**8**.

obtained residue **4** corresponded to a 30% weight loss from **2** and contained more than 6% remaining carbon.

The ^{13}C and ^{29}Si CP MAS NMR spectra were consistent respectively with the presence of sp^2 carbon atoms and of SiO_4 substructures in the solid material **4** (Figure 7). The elimination of carbon was obtained upon an additional thermolysis of **4** in air. Heating at 550 °C for again 4 h gave a (SiO_2) residue **5** after a total weight loss of 38%. This value is consistent with the complete elimination of the C and the conservation of Si in a solid having the initial stoichiometry of gel **2**. The analysis revealed 0.8% carbon, but no resonance was visible in the ^{13}C NMR spectra. The ^{29}Si CP MAS spectrum showed signals only at −103.6 and −110.0 ppm (SiO_4, Q^3 and Q^4 substructures) and was indicative of a highly condensed silica material (Figure 7). The characterization of the surface properties of the solids **4** and **5** was also performed (cf. Table 1, entries c, d). **4** and **5** presented very similar N_2 BET surface areas (348 and 333 m^2 g^{-1}, respectively), pore volumes, and mean pore diameters. The values were lower than those found in the case of the nonpyrolyzed gel **2**.

The pyrolysis in air of the solid **3**, arising from the thermolysis of gel **2** at 200 °C and containing ene—yne cross-linking units, was also studied (eq 7). Heating

3, R = H or Me
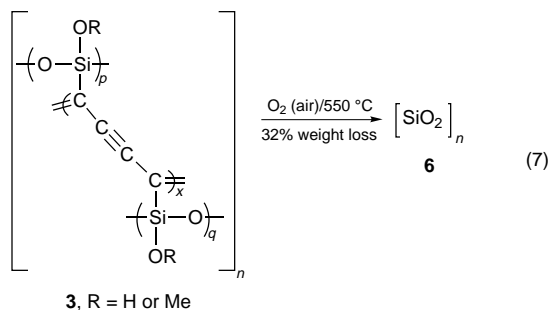
under an O_2 flow at 550 °C for 4 h caused a 32% weight loss to give the new solid **6**. It contained no carbon, and the ^{29}Si CP MAS NMR spectra showed only resonances of SiO_4 substructures (Figure 7). The solid-state properties of the amorphous silica material **6** were similar to those observed for the solids **4** and **5** arising from the high-temperature oxidation of **2**. Similar surface area and pore volume were measured (cf. Table 1, entry

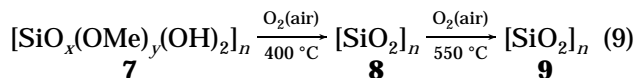e). The gel **2** with bridging diyne units probably thermally cross-linked through ene−yne formation in a first step, and then oxidative decomposition took place. Thus the routes to silica in eqs 6 and 7 are quite similar.

Nucleophilic Cleavage of the Si−C Bond in Gel 2. The use of the reactive Si−C bond in gel **2** is also of interest since it should allow us to prepare silica material under reaction conditions much milder than using the thermolysis under O_2. The elimination of the organic diyne unit was achieved upon treatment with methanol/water in the presence of fluoride ion catalyst.[4,8] Thus the gel **2** was stirred in methanol with an excess of H_2O in the presence of 2 mol % of NH_4F catalyst (eq 8). After drying, the new solid **7** was obtained in a 73% yield. As expected from the partial weight loss (27%), **7** contained ca. 5% carbon as determined by elemental analysis. However, the ^{13}C CP MAS NMR spectrum indicated that all the acetylenic carbon were eliminated. The single ^{13}C resonance observed at 49 ppm is due to residual methoxy groups in the partially condensed material. The ^{29}Si CPMAS NMR spectrum also showed the expected set of resonances characteristic of SiO_4 substructure (Figure 7). Thus, no Si−C bond remained in the solid. Moreover, the major [29]Si resonance observed at −100.2 ppm and assigned to a Q^3 Si(OR)(OSi≡)$_3$ substructure, is in agreement with the presence of many uncondensed groups in the silica material. Also consistently, the TGA analysis of **7** only revealed a weight loss between 100 and 200 °C which was attributed to the desorption of solvent molecules. Interestingly, the elimination of the organic moiety under mild reaction conditions (eq 8) led to a material with a very high surface area. N_2 BET measurements for **7** revealed a 905 $m^2\,g^{-1}$ surface area and a pore volume of 0.66 mL g^{-1}.

$$\left[\begin{array}{c} OR \\ | \\ +(O-Si)+_p \\ | \\ C \\ ||| \\ C \\ | \\ C \\ ||| \\ C \\ | \\ +(Si-O)+_q \\ | \\ OR \end{array} \right]_n \xrightarrow[\text{NH}_4\text{F}]{\text{H}_2\text{O/MeOH}} \left[SiO_x(OMe)_y(OH)_z \right]_n \quad (8)$$

7

2, R = H or Me
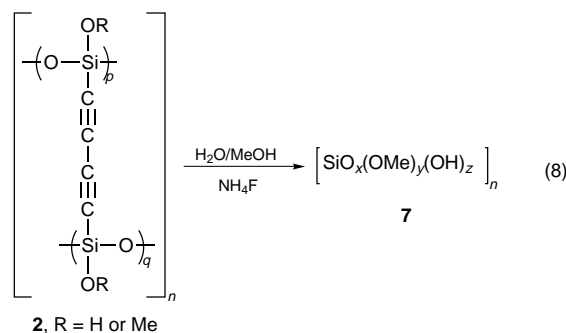
The complete elimination of the residual methoxy groups in the solid **7**, to give an almost carbon free silica material, was performed upon heating in air (eq 9). The

$$[SiO_x(OMe)_y(OH)_2]_n \xrightarrow[\text{400 °C}]{\text{O}_2\text{(air)}} [SiO_2]_n \xrightarrow[\text{550 °C}]{\text{O}_2\text{(air)}} [SiO_2]_n \quad (9)$$
$$\quad\quad\text{**7**}\quad\quad\quad\quad\quad\quad\text{**8**}\quad\quad\quad\text{**9**}$$

thermolysis at 400 °C for 4h, yielded the new solid **8**. The latter gave no signals in ^{13}C NMR and when compared to **7**, more intense resonances were observed at −100 and −110 ppm in the ^{29}Si NMR spectrum (Figure 7). This is indicative of a higher degree of condensation in **8** than in the initial solid **7**. The thermolysis at 400 °C did not produce significant change in the solid-state properties. A 980 $m^2\,g^{-1}$ N_2 BET surface area was found and essentially no change were noted in the pore volume and mean pore diameter (cf. Table 1 entry g). To have a better comparison with the silica materials **4**−**6**, resulting from the calcination of

Scheme 2. Removal of the Organic Fragments in Hybrid Gel 2
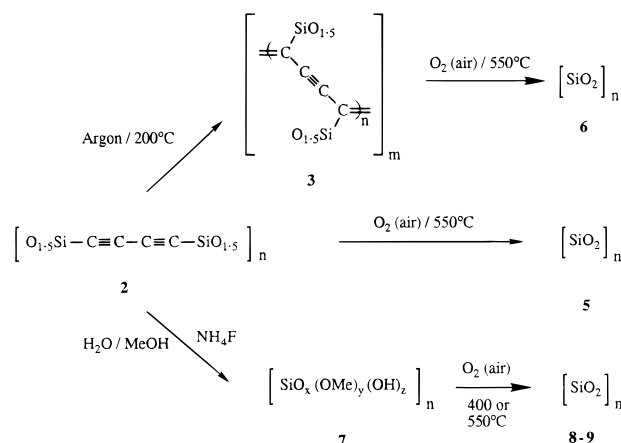
2 and **3**, the solid **8** was further pyrolyzed in air at 550 °C for 4 h. This treatment caused no weight loss and gave **9** with spectroscopic characteristics identical with those of **8**. Compared to the latter, a small decrease (ca. 10%) in the N_2 BET surface area and pore volume was measured for **9** (Table 1, entry h).

The chemical or oxidative cleavages of the Si−C bond, leading to the elimination of the organic moiety in hybrid gel, gave silica materials with different BET surface area and pore volumes (cf. Table 1). For comparison, the various treatments of the hybrid gel are summarized in Scheme 2. The silica gels **5** and **6**, arising from the pyrolysis of **2** in air, exhibited reduced N_2 BET surface area and pore volume with respect to those measured for the initial hybrid gel **2** (cf. Table 1, entries c−e). The thermal oxidation causes some rearrangements in the silicate network and gives material with a lower porosity. The elimination of the organic bridging fragment under mild reaction conditions, led to material **7**, with much higher surface area and porosity than those of **2** (entries f, h). **7** is quite thermally stable, a second pyrolysis in air at 550 °C did not cause a large decrease in surface area and pore volume. The nucleophilic cleavage of the Si−C bond at comparatively low temperature probably produces less alterations of the inorganic framework and allowed to obtain silica with increased BET surface area and pore volume. It is also interesting to note that the solid can present different properties while the ^{29}Si NMR revealed that in some cases the inorganic network presents similar degree of condensation (Figure 7).

Our observations show that different silica materials can be produced, from a single hybrid organic−inorganic silsesquioxane, according to the way that is used to remove the organic component. It appeared here that porous material with different properties resulted from modification of the molecularly defined network. A related approach involving the incorporation of sacrificial organic template molecules within the silica matrix, has been recently reported.[10−13] Hydrocarbon spacers in polysilsesquioxanes were removed by oxidation upon thermolysis or by use of an oxygen plasma. The cleavage of Si−C sp bonds, under mild reaction conditions is of particular interest since it allows a smooth removal of the organic moiety and gives rise to silica with a porosity much higher than that produced upon thermal oxidation of the hybrid precursor.

Conclusion

The sol−gel polycondensation of (MeO)₃SiC≡CC≡CSi-(OMe)₃ readily leads to a network consisting of alternating siloxane and diyne units. Silica gels containing 1,3-butadiyne bridging fragments constitute a highly reactive class of hybrid material.

The diyne unit was shown to polymerize upon thermolysis of the amorphous material. Although some Si−C bond cleavage occurred, it formed in the inorganic solid, an organic polymer containing ene−yne chain units attached to the silica framework. The polymerization, observed in the solid state, suggests favorable arrangements of the organic fragments within the amorphous solid. The resulting composite material may be described as a network made of interpenetrating ene−yne and silicate polymers.

The organic component of the hybrid diyne silica gel could be removed either via thermal oxidation at 550 °C or via a smooth solid−liquid reaction of cleavage of the Si−C bond. It gives rise to porous silica materials with differences according to the reaction conditions. The facile nucleophilic cleavage of Si−C bond opens some possibility to prepare inorganic solid from molecularly defined hybrid materials. We are currently investigating a possible control of the solid morphology based on the size and structure of the molecular precursor.

Experimental Section

All manipulations, carried out under nitrogen or air, were performed using dried gas. Solvents were also dried and distilled before use. The IR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrometer. The solid-state cross-polarization/magic angle spinning (CP/MAS) ^{29}Si and ^{13}C NMR spectra were obtained on a Bruker FT AM 300 apparatus. ^{13}C NMR: NMR frequency, 75.47 MHz; recycling delay, 1 s; contact time, 5 ms; acquisition time, ca. 20 000 scans, spinning rate 500 Hz. ^{29}Si NMR: NMR frequency, 59.62 MHz; recycling delay, 10 s; contact time, 2 ms; acquisition time, ca. 300−7000 scans, spinning rate 5000 Hz. X-ray powder diffraction measurements were performed using a Seifert MZ 4 apparatus. Differential scanning calorimetry (DSC) experiments were performed under argon on a Mettler 30 instrument at a heating rate of 5 °C/min. Polymer molecular weight was characterized by using a Waters 510 instrument with UV and refractive index detection. Polystyrene standards were used to estimate weight average and average molecular weights number. The porosities of the columns used were 100, 500, 10³, and 10⁴ Å, and the elution rate of THF, which was used as solvent, was 1 mL min⁻¹. Thermogravimetric analyses (TGA) were performed under flowing air or argon (50 mL min⁻¹) with a Netzsch STA 409 thermobalance, the typical heating rate being 10 °C min⁻¹. The pyrolysis experiments, performed with a Eurotherm furnace, were carried out by pouring weighed samples of solids into an aluminium oxide boat placed in an aluminum oxide tube connected to a vacuum line. The gas flow was maintained around 50 mL min⁻¹ during pyrolysis. Elemental analyses were carried out by the "Service Central de Micro-Analyse du CNRS".

1,4-Bis(trimethoxysilyl)-1,3-butadiyne (1). This compound was prepared according to a literature procedure.[9]

Hydrolysis and Polycondensation of 1,4-Bis(trimethoxysilyl)-1,3-butadiyne (1). To a mixture of **1** (2.87 g, 9.87 × 10⁻³ mol) in 9.9 mL of MeOH were added 9.87 × 10⁻⁶ mol (0.1%) of NH₄F and 2.96 × 10⁻² mol (3 equiv) of water. The gel obtained after 10 min was allowed to stand at room temperature for 48 h. After washing with ether and drying

under vacuum at room temperature, about 1.5 g of a white powder **2** was collected. FT-IR (KBr) 2045, 2091, 2202, 2845, and 3295 cm⁻¹. ^{13}C CP MAS NMR (δ, ppm) 52.4, 79.4, 87.8. ^{29}Si CP MAS NMR (δ, ppm) −80.7, −89.9, −99.5. Anal. Found: C, 26.80; H, 1.48; Si, 28.31. Calcd carbon-to-silicon ratio for C₄O₃Si₂ C/Si = 2; found C/Si = 2.2. X-ray powder diffraction: two broad bands, *d* spacing 3.9 and 8.0 Å. DSC analysis: broad exothermic peak centered at 175 °C. N₂ BET surface area: 467 m² g⁻¹. Average pore diameter: 32 Å.

Thermal Treatment of 2 in an Inert Atmosphere. By heating 2.1 g of compound **2** at 200 °C (heating rate 10 °C min⁻¹) for 4 h under a nitrogen flow, 2.0 g of a brown powder **3** was obtained. FT-IR (KBr) 2092, 2169, 2202 cm⁻¹. ^{13}C CP MAS NMR (δ, ppm) 133 (very broad). ^{29}Si CP MAS NMR (δ, ppm) −60.0 to −80.0 (very broad), −91.0, −100.2, −110.1. Anal. Found: C, 24.68; H, 1.57; O, 32.29; Si, 27.51. Calcd carbon-to-silicon ratio C/Si = 2; found C/Si = 2.1 N₂; BET surface area 216 m² g⁻¹. Mean pore diameter 37 Å.

Pyrolysis of Compound 2 in Air Atmosphere. Calcination under an air flow at 400 °C (heating rate 2 °C min⁻¹) for 4 h of compound **2** (0.3 g, 1.97 × 10⁻³ mol) led to 0.21 g of a light yellow powder which was characterized. ^{13}C CP MAS NMR (δ,ppm) 130.4. ^{29}Si CP MAS NMR (δ, ppm) −91.3, −99.9; −108.5. Anal. Found: C, 6.38; H, 1.44; 0.51.71; Si, 43.39. N₂ BET surface area 348 m² g⁻¹. Mean pore diameter 26 Å. To eliminate residual carbon and hydrogen, the solid **4** was then heated again in air at 550 °C for 4 h. The white powder **5** (0.19 g) was obtained. ^{13}C CP MAS NMR, no signal. ^{29}Si CP MAS NMR (δ, ppm) −103.6, −110.0. Anal. Found: C, 0.79; H, 0.30; 0.51.83; Si, 45.63. N₂ BET surface area 333 m² g⁻¹. Mean pore diameter 27 Å.

Pyrolysis of Compound 3 in Air. The solid **3** (2 g, 1.32 × 10⁻² mol) was calcinated under air flow at 550 °C for 24 h. (heating rate to reach 550 °C: 2 °C min⁻¹). A weight loss of 32.0% was observed and 1.35 g of white powder **6** were obtained. ^{13}C CP MAS NMR, no signal. ^{29}Si CP MAS NMR (δ, ppm) −92.0, −100.5; −113.5. Anal. Found: C, 0.21; H, 2.48; O, 54.87; Si, 44.35. N₂ BET surface area 302 m² g⁻¹. Mean pore diameter 30 Å.

Reaction of 2 with MeOH/F⁻. In a flask equipped with a magnetic stirrer and a condenser were placed 2.6 g (1.71 × 10⁻² mol) of solid **2**, 50 mL of MeOH, 2% (3.4 × 10⁻⁴ mol) of NH₄F, and 6 mL (20 equiv) of water. After stirring for 72 h at 64 °C, the mixture was filtered. The solid thus obtained was washed with ether and dried in vacuo at room temperature to afford 1.89 g (73% w/w yield) of the colorless powder **7**. ^{13}C CP MAS NMR (δ, ppm) 49.0. ^{29}Si CP MAS NMR (δ, ppm) −91.5, −100.2, −108.6. Anal. Calcd for SiO₂: O, 53.33; Si, 46.67. Found: C, 5.31; H, 2.73; O, 41.29; Si, 34.75. X-ray powder diffraction: one broad band, *d* spacing 3.75 Å. N₂ BET surface area: 905 m² g⁻¹. Mean pore diameter: 29 Å. As the TGA analysis of **7** under air flow from 20 to 1000 °C exhibits only a weight loss of 18% between 100 and 200 °C. The solid **7** was first calcinated in an air flow at 400 °C for 4 h (heating rate 10 °C min⁻¹) and then characterized. ^{13}C CP MAS NMR, no signal. ^{29}Si CP MAS NMR (δ, ppm) −92.0, −100.1, −110.0. Anal. Found: C, 0.70; H, 1.09; O, 58.20; Si, 41.03. The N₂ BET surface area was then 950 m² g⁻¹, and the mean pore diameter 29 Å. The white powder **8** was finally heated at 550 °C for 4 h under air flow. The new solid **9** was collected. As expected from TGA analysis, no weight loss was observed. ^{13}C and ^{29}Si NMR spectra of the solid **9** were identical to those of **8** described above. Elemental Anal. Found: C, 0.20; H, 0.50; O, 54.37; Si, 46.00. N₂ BET surface area 800 m² g⁻¹. Mean pore diameter 28 Å.

Supporting Information Available: Cumulative pore volume and pore area plots, *T* plot and pore volume distribution curves as a function of pore diameter (72 pages). Ordering information is given on any current masthead page.