Generation of Carbonaceous Structures in Silica Aerogel

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Pyrolysis of organically substituted aerogels of the idealized composition $R_{0.2}SiO_{1.9}$ (R = CH_3, C_6H_5, $CH{=}CH_2$, C_3H_7) in a standing atmosphere of argon results in the formation of carbonaceous structures covering the inner surface of the aerogels. This results in a very high infrared opacification (high specific extinction) of the aerogels necessary for high-temperature (200–500 °C) thermal insulation. The development of the carbon structures during pyrolysis was followed by infrared spectroscopy and elemental analyses. The carbon content and the percentage of retained carbon depend very much on the kind of organic groups and the density of the starting aerogels. The best results with regard to carbon incorporation, specific extinction and retention of the aerogel structure were obtained by pyrolysis of $Ph_{0.2}SiO_{1.9}$. A higher portion of organic groups in the aerogels also results in a higher retention of carbon. The temperature necessary for complete pyrolysis depends on the density of the aerogels. Aerogels with initial densities of 200–300 kg m^{-3} are completely pyrolyzed at 1000 °C, while those with an initial density <150 require only 700 °C. The structure of the aerogels (pore sizes and diameters, specific surface area) is not severely changed by the pyrolysis; however, there is a slight net increase of the density. Additional carbon can be incorporated, and the specific extinction can be considerably increased by holding the pyrolyzed aerogels at 1000 °C in a CH_4/Ar atmosphere.

Introduction

Silica aerogels have interesting applications, among them as thermal insulation materials. Due to their low density and small pore radii, the heat transport via the solid aerogel skeleton and the gas phase is low. The radiative transport below 20 °C is also low, because silica aerogels absorb heat sufficiently. However, use of silica aerogel for heat insulation at medium temperatures (50–500 °C) requires reduction of the radiative heat transport. The reason for this is that the radiation maximum at these temperatures is at 2–8 μm, where silica has a low specific extinction (1 m^2 kg^{-1}). Carbon black is very well suited for infrared opacification due to its broad absorption band in the relevant range. It was shown that the quantity of added carbon black is important for not only the quality of the infrared opacification but also the structure, size and agglomeration of the carbon particles.[1,2]

Mixing aerogel powders with 20% carbon soot increases the specific extinction in the range 2–8 μm to a sufficient value of 100–200 m^2 kg^{-1} (specific thermal conductivity 0.018–0.020 W m^{-1} K^{-1}). One disadvantage of this approach, however, is the handling of powders. Furthermore, it is not possible to further increase the specific extinction by a higher portion of soot. Specific extinction depends on the particle size, and a maximum is predicted for carbon spheres of 1.5 μm diameter. For larger (agglomerated) particles, which are more easily formed with a higher soot portion, extinction decreases proportional to the diameter.[3]

Another possibility to achieve infrared opacification is the addition of soot already during sol–gel processing. This approach has the same limitations concerning extinction. Additional problems arise from sedimentation of the soot particles and their influence on the formation of the gel nanostructure.

Our approach, which is void of these problems, is to generate carbonaceous structures in silica aerogels either by pyrolysis of organically modified aerogels[4,5] or by pyrolysis of gaseous organic compounds (see refs 5 and 6 for preliminary results). While our work was in progress, Hunt et al. also reported the preparation of carbon particles in silica aerogels by pyrolysis of organic gases.[7] Several studies on the pyrolysis chemistry of siloxane materials have been published,[8] but none of them with the goals of our work.

The structure of a silica aerogel prepared by base-catalyzed hydrolysis and condensation of $Si(OR)_4$ is shown in Figure 1.[9] It consists of secondary particles of about 5 nm diameter composed of smaller primary particles. In unmodified aerogels residual Si–OH groups are located at the surface of the primary particles. We have recently prepared organically modified silica aero-

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[®] Abstract published in *Advance ACS Abstracts,* September 1, 1995.

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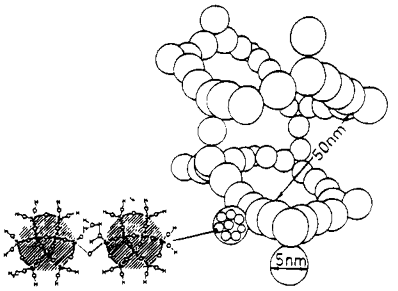

Figure 1. Structural model of a silica aerogel prepared by base-catalyzed hydrolysis and condensation of $Si(OR)_4$.

gels by NH_4OH-catalyzed hydrolysis and condensation of $RSi(OMe)_3/Si(OMe)_4$ mixtures (R = alkyl, alkenyl, or aryl), followed by supercritical drying of the alcogels with methanol or CO_2.[4,5] Incorporation of up to 20% $RSiO_{3/2}$ units into the aerogels only slightly diminished the transparency and porosity relative to unmodified silica aerogels, while the elastic constant was significantly lowered. We showed that in the organically modified aerogels the organic groups R are mainly located at the *surface* of the primary particles having a SiO_2 core. They do not disturb the basic aerogel structure, and therefore the typical aerogel properties are retained. Since they replace Si−OH groups, the organically modified aerogels are hydrophobic.

For an effective infrared opacification a homogeneous distribution of the carbon structures is very important.[1,2] Ideally, the inner aerogel surface should be uniformely covered by carbon. Since the organic groups in the organically modified aerogels already are located there, their pyrolysis should be the best approach to achieve a homogeneous distribution of carbon. Furthermore, the equal distribution of the organic groups on the inner surface should result in a great number of well-distributed nucleation centers during pyrolysis and thus also lead to small carbon particles. There should be no diffusion problems, which could arise upon pyrolysis of gaseous organic compounds in the aerogels.

In this article we focus on how the yield and structure of the carbon particles are optimized by the proper choice of the starting compounds and the conditions of the pyrolysis process. The thermal conductivity properties of the thus-prepared silica/carbon aerogels were already reported.[2,10] These studies show that our method is very efficient for infrared opacification. Due to the arrangement of the carbon structures generated during pyrolysis, a smaller amount of carbon results in an efficient extinction. Thus, a specific extinction of 73 $m^2\ kg^{-1}$ at 2.5 μm was obtained for an aerogel with a density of 322 $kg\ m^{-3}$ containing 14 wt % carbon.[10] The extinction is even higher for analogous aerogels with a lower density (for instance, 180 $m^2\ kg^{-1}$ at 2.5 μm for an aerogel with 110 $kg\ m^{-3}$ containing 8.5 wt % carbon).[11] It can increased by a factor of 5−10 to nearly 1000 $m^2\ kg^{-1}$ by treatment of the pyrolyzed aerogels in a CH_4/Ar atmosphere at 1000 °C.[2]

Results and Discussion

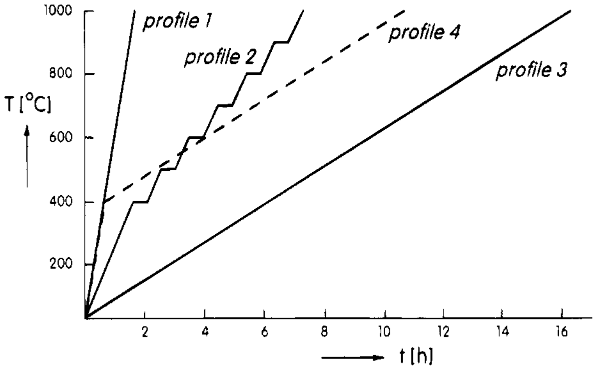

Figure 2. Temperature profiles for the pyrolysis of the aerogels.

Table 1. Properties of Pyrolyzed Me20 (Accuracy ±10−15%)

	profile 1	profile 2	profile 3	profile 4
carbon content (wt %)	2.6	1.8	2.6	2.6
% retained carbon	35	24	35	33
hydrogen content (wt %)	0.3			
Si−H band in the infrared	yes	no	no	no
spec surface area [$m^2\ g^{-1}$]	537	404	487	444
% of the specific surface area relative to unpyrolyzed sample	93	69	84	78

The organically modified SiO_2 aerogels used in this work for pyrolysis were prepared as previously described (dried by supercritical methanol)[4,5] and had densities between 210 and 280 $kg\ m^{-3}$, if not otherwise stated. The following acronyms will be used: **00**, idealized composition SiO_2; **Me20**, $(CH_3)_{0.2}SiO_{1.9}$; **Me40**, $(CH_3)_{0.4}SiO_{1.8}$; **Vi20**, $(CH_2{=}CH)_{0.2}SiO_{1.9}$; **Pr20**, $(CH_3CH_2CH_2)_{0.2}SiO_{1.9}$; **Ph20**, $(C_6H_5)_{0.2}SiO_{1.9}$.

Preparation, composition (the real composition slightly deviates from the idealized one, due to residual OH and OMe groups), structures, and properties of the starting aerogels are described elsewhere.[4,5]

Optimization of the Pyrolysis Process. The feasibility of carbon generation in silica aerogels by pyrolysis of the organically modified aerogels was initially carried out in a slightly flowing stream of argon. However, this resulted in the complete removal of all carbon as gaseous products. In subsequent experiments the aerogels were therefore heated to 1000 °C in a standing atmosphere of argon (i.e., the aerogels were heated in an atmosphere of Ar without removing the gas phase during heating). Under these conditions, the aerogel **Me20** with a starting density of about 200−300 $kg\ m^{-3}$ becomes yellowish at about 600 °C. Upon further increase of the temperature, the color continuously intensifies to brown and finally black. We attribute the fact that no carbon is deposited in a flowing stream of carbon to the open porosity of aerogels. A stream of Ar obviously removes the hydrocarbons formed in the initial stage of the pyrolysis. These hydrocarbons are needed for the growth of the carbon structures (see below).

The effect of different heating rates (Figure 2) on the properties of the pyrolyzed aerogel **Me20** is shown in Table 1.

Infrared spectra and elemental analyses clearly show that rapid heating to 1000 °C (profile 1) does not result in the complete pyrolysis of all organic groups. There are two characteristic OH bands (3734 and 3663 cm^{-1}), a broad band of absorbed water (3400−3500 cm^{-1}), a SiH band at 2281 cm^{-1}, and small CH bands in the

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(10) Kuhn, J.; Schwertfeger, F.; Arduini-Schuster, M. C.; Fricke, J.; Schubert, U. *J. Non-Cryst. Solids* **1995**, *186*, 184.

(11) Schwertfeger, F. Ph.D. Thesis, University of Würzburg, Germany, 1994.

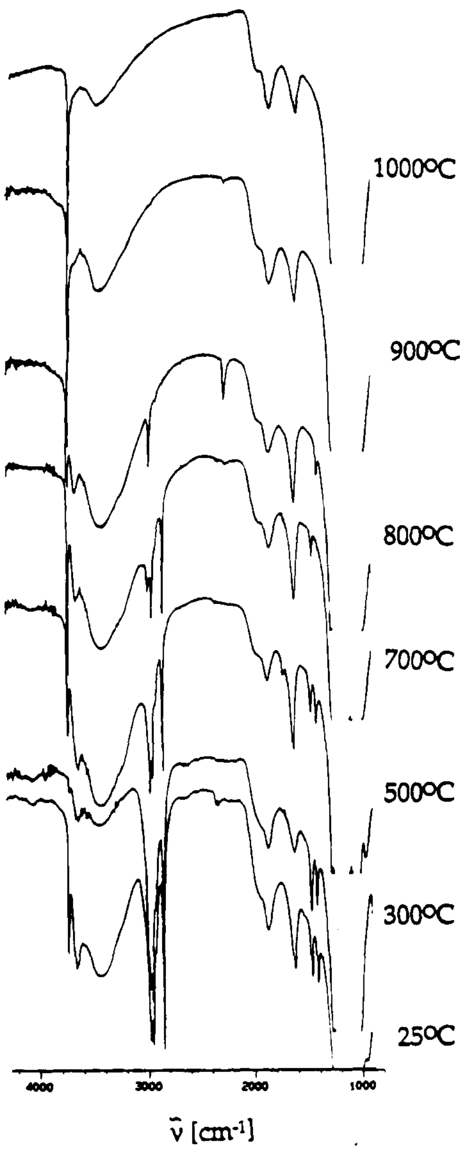

Figure 3. Infrared spectra of **Me20** aerogel pyrolyzed at the indicated temperatures (temperature profile 3).

range 2860–3000 cm^{-1}. These features are missing when temperature profiles 2 or 3 are used. Temperature profile 3 is preferred over profile 2 because a higher percentage of carbon (35% of the original carbon content) and a higher surface area is retained. Since the heating rate at low temperatures does not affect the final proproperties of the pyrolyzed aerogels, profile 4 (10 °C/min up to 400 °C, then 1 °C/min) was used for all later reactions, to shorten the pyrolysis period.

To monitor the pyrolysis process, FTIR spectra were recorded from **Me20** aerogel samples taken from the oven in regular temperature intervals (Figure 3). The results are very similar to those observed for xerogels derived from $CH_3Si(OR)_3$[12] or $(CH_3)_2Si(OR)_2$.[8] **Me20** is rather stable up to 400 °C; the CH bands of the CH_3 and (residual) OCH_3 groups at 1465, 1408, 2979, and 2861 cm^{-1} are unchanged. A decrease in intensity of the water band at 3400–3500 cm^{-1} and the SiOH band at 3734 cm^{-1} indicates desorption of water and the beginning of the surface site condensation processes.

Table 2. C, H, Si Elemental Analyses at Different Stages during the Pyrolysis of Me20 (Temperature Profile 3)

temp [°C]	% C	% H	% Si	C:H	C:Si
25	7.67	1.71	43.5	1:2.7	1:2.4
200	7.34	1.61		1:2.6	
300	6.53	1.54		1:2.8	
400	4.07	1.27		1:3.7	
600	3.11	0.87	44.5	1:3.3	1:6.1
700	3.04	0.90	44.2	1:3.5	1:6.2
800	2.49	0.54		1:2.6	
850	3.64	0.35		1:1.2	
900	3.56	0.24	45.3	1:0.8	1:5.5
1000	2.59	0.00	45.2	1:0	1:7.5

Between 400 and 700 °C, rearrangement processes occur.[10] Additionally, SiOMe groups are converted into SiOH groups, as indicated by the decrease of the OMe bands and increase of the SiOH bands at 3734 and 3691 cm^{-1}. Both processes result in changes of the siloxane skeleton. Final degradation of the organic groups occurs above 700 °C, indicated by the further decrease of the CH bands and the intermediate occurrence of SiH bands.

Since **Me20** changes its color only above 600–700 °C, no carbon particles are formed below this temperature. The analytically determined C:H ratio (Table 2) is rather constant up to 300–400 °C (it is not 1:3 due to the large absolute error in the analytical values for hydrogen), while the C:Si ratio decreases. This indicates the cleavage of gaseous products containing CH_3 groups. Raising the temperature above 300 °C results in an increase of the C:H ratio due to the formation of SiOH and SiH species from SiMe. Above 700 °C degradation occurs via formation of C_nH_m species with a lower C:H ratio. These are successively transformed into carbon (the possibility that carbon structures are already formed while C_nH_m species are still present is of course also possible). At 1000 °C the hydrogen concentration is below the detectable limit. We cannot totally exclude the possibility that structures with Si–C bonds are also present after pyrolysis. However, if this is the case, they do not show up in the physical and materials properties of the final aerogels, which are sufficiently explained by only a carbon phase. The solid-state ^{13}C and ^{29}Si NMR spectra of the pyrolyzed aerogels also shown no signals which can be attributed to Si–C containing groups. The only peak in the ^{29}Si MAS-NMR spectrum is that of SiO_2.

The homogeneous distribution of carbon is a prerequisite for an effective reduction of the radiation transport in the infrared range, which is also influenced by both size and structure of the carbonaceous particles. The kind and concentration of the organic groups in the starting aerogels were expected to be an important issue for optimizing the pyrolysis process, because (i) depending on the kind of organic groups, the initial carbon concentration is different, and (ii) alkyl or aryl groups provide a different starting situation for the structural development of the carbonaceous particles.

Table 3 shows several trends:

(i) With an increasing number of carbon atoms in the organic groups R of the starting aerogel, the *carbon content* in the pyrolyzed aerogels increases. In the series of aerogels having the starting composition $R_{0.2}SiO_{1.9}$ (20% of the silicon atoms being substituted by an organic group) and densities of 230–290 kg m^{-3} the carbon concentration after pyrolysis increases from 2.6%

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(12) Kamiya, K.; Yoko, T.; Tanaka, M.; Takeuchi, M. *J. Non-Cryst. Solids* **1990**, *121*, 182. Kamiya, K.; Yoko, T.; Sano, T.; Tanaka, M. *J. Non-Cryst. Solids* **1990**, *119*, 14.

Table 3. Carbon Content (by Elemental Analysis, ±10%) in the Pyrolyzed Aerogels (Values in Brackets Are the Percentages of Retained Carbon)

	starting density [kg m^{-3}]	starting carbon content	pyrolysis temp [°C] 700	900	1000
00	267	5.33			1.92 (36)
Me20	237	7.83			2.59 (33)
Me40	208	9.81			6.18 (63)
Vi20	265	9.98			5.72 (57)
Pr20	230	10.62			8.98 (85)
	134	11.65	5.09 (44)	4.61 (40)	4.17 (36)
Ph20	288	19.29			13.92 (72)
	151	18.12	12.48 (69)	11.83 (65)	12.10 (67)
	87	18.34	11.15 (61)	10.84 (59)	8.52 (47)

Table 4. Density [kg m^{-3}] Changes upon Pyrolysis (Values in Brackets Are the Percent Increase in Density Relative to the Starting Density)

	starting density	holding time at 1000 °C[a] 0 h	5 h	10 h
00	267	281 (5)		
Me20	256	276 (8)	280 (9)	299 (17)
Me40	210	239 (14)		
Vi20	265	395 (49)	407 (54)	437 (65)
Pr20	230	274 (19)		
Ph20	278	307 (10)	325 (17)	331 (19)
	151	178 (18)		
	87	110 (26)		

[a] Time for which the aerogel was *additionally* held at 1000 °C after the pyrolysis process.

Table 5. Changes of the Specific Surface area [m^2 g^{-1}] upon Pyrolysis (Values in Brackets are the Percent Decrease of the Surface Area Relative to the Starting Surface Area)

	starting surface area	hold time at 1000 °C[a] 0 h	5 h	10 h
00	470	412 (12)		
Me20	566	444 (22)	368 (35)	338 (40)
Me40	610	394 (35)	420 (31)	317 (48)
Vi20	590	403 (32)	358 (39)	339 (43)
Pr20	505	331 (35)	348 (31)	322 (36)
Ph20	500	320 (36)	359 (28)	296 (41)

[a] Time for which the aerogel was *additionally* held at 1000 °C after the pyrolysis process.

for R = CH_3 to 9.0% for R = C_3H_7. It further increases to 13.9% for R = C_6H_5, due to the larger number of carbon atoms and the aromatic nature of this group.

(ii) The percentage of *retained carbon* also depends on the kind of R. More than 60% of the carbon is lost during pyrolysis of the unsubstituted aerogel **00** (which contains residual methoxy groups as the carbon source) or **Me20**. The retained carbon portion is much higher with larger organic groups, with maximum values for R = propyl (85%) and R = phenyl (72%).

(iii) An increased portion of organic groups in the starting aerogel (for instance, **Me20** vs **Me40**) also results in a higher retention of carbon.

(iv) Decreasing the density of the aerogels results in a larger loss of carbon. This is understandable, since porosity of the aerogels increases with decreasing density. The gaseous hydrocarbons formed upon hydrolysis therefore can diffuse more easily out of the material.

In conclusion, to achieve a high carbon content in the pyrolyzed aerogels and to retain a large percentage of the carbon during pyrolysis, aerogels substituted with large organic groups, preferentially aromatic groups, should be used. The alternative possibility of increasing the portion of the organically substituted silicon atoms in the starting aerogels is less suitable, because this portion cannot be raised as high as necessary without destabilizing the aerogel structure.[4a,b]

There is a very interesting phenomenon about the temperature necessary to pyrolyze all organic groups. It gets lower with decreasing density of the aerogels. The phenyl- or propyl-substituted aerogels with densities smaller than 150 kg m^{-3} *are completely pyrolyzed at 700 °C*. Already at this temperature no hydrogen can be detected any longer by elemental analyses, and there are no C−H vibrations in the infrared spectra.

Once the organic groups are pyrolyzed, there is no further loss of carbon. Holding selected samples at 1000 °C up to 10 h did not result in a detectable decrease of the carbon content.

Structural Investigations. The heat treatment of the aerogels affects not only the organic groups but also the silica skeleton. Since structural rearrangements would influence the heat transport through the pores or along the silica skeleton, attention has to be paid to this issue.

Density changes are listed in Table 4. When the starting density is compared with the density of the aerogel bodies after pyrolysis, two processes with opposite influence on the macroscopic density have to be considered. The samples get denser by sintering processes (volume decrease), but they lose mass by the evolution of water and hydrocarbons (mass decrease). The net result, however, is a higher density in each sample. In the series of aerogels having the starting composition $R_{0.2}SiO_{1.9}$ the density increase is lowest for the R = methyl. There is no obvious dependency on the nature of the organic group. We have currently no explanation for the very large density increase of the vinyl-substituted aerogel. The rather low density increase of **Ph20** is another reason this aerogel should be preferentially used for infrared opacification by pyrolysis. Higher concentrations of organic groups in the starting aerogel and lower densities promote densification during pyrolysis.

When the aerogels are held at 1000 °C after pyrolysis, density decreases continuously due to sintering.

N_2 adsorption (BET method) reveals that the pore shape (mainly open, cylindrical pores) and the pore size distribution do not change significantly during pyrolysis. The *C* value, a substrate-specific constant in the BET equation, describes the interaction of the adsorbate with the substrate surface. It is in the range of 100 for very polar surfaces and decreases with decreasing polarity down to about 30.[13] In organically substituted aerogels the *C* value is around 50, i.e., the surfaces are nonpolar. During pyrolysis it increases to about 80−100, i.e., by the pyrolysis reactions the surface gets very polar. Due to the formation of the carbon structures, the specific surface area of the pyrolyzed aerogels (i.e., the silica/carbon composite, where one cannot differentiate between the silica surface and the carbon surface) is smaller than that of the starting aerogels (Table 5). Holding the aerogels at 1000 °C after pyrolysis does not severely affect the surface area.

Small-angle X-ray scattering (SAXS) investigations showed that the size of both the primary and secondary

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(13) Lowen, K. W.; Broge, E. C. *J. Chem. Phys.* **1961**, *65*, 16.

particles remains constant during pyrolysis and holding at 1000 °C. The unmodified silica aerogel **00** has a smooth surface (surface roughness $D_s = Kq^{3.9}$). Organic modification results in a rougher surface ($q^{3.1-3.3}$).[5] During pyrolysis the surface gets smooth again, due to the degradation of the organic groups ($q^{3.8-3.9}$ after complete pyrolysis). Therefore, the effect of the organic groups on the appearance of the SAXS curves is canceled upon pyrolysis, and the SAXS curves of the carbon-doped aerogels are basically the same as those of unmodified SiO_2 aerogels.

The overall result of the structural investigations is that the typical aerogel nanostructure is basically retained during degradation of the organic groups and formation of the carbonaceous structures. This is also supported by scanning transmission electron micrographs (TEM), which show no difference between the unpyrolyzed and the pyrolyzed aerogels. In both cases there are secondary particles in the range 5–10 nm and pores of 20–50 nm. Since no morphologically new particles can be detected, the carbon must either have the same morphology as the silica particles or it is highly dispersed as a sheath over the silica skeleton. The latter possibility is more likely. It is supported by the SAXS curves of the pyrolyzed aerogels, which show a interference structure at large scattering vectors ($q \geq 0.2$ Å^{-1}). This is a hint for the formation of new structures in the subnanometer range.[10] However, these effects are at the lower limit of the method; a more precise size determination is therefore not possible.

We have previously reported a Raman spectrum of the pyrolyzed aerogel **Ph20**, showing two bands at 1596 and 1292 cm^{-1}.[2,5,10] These bands are characteristic for crystalline and amorphous carbon.[14] The intensity ratio of both bands is approximately 1, which means that both phases are present in equal amounts. Holding the pyrolyzed aerogels at 1000 °C does not change the intensity ratio and therefore the carbonaceous structures. XRS shows only the lines of graphitic carbon.

We conclude from these observations that the carbon structures generated during pyrolysis cover part of the silica nanospheres, from which the aerogel skeleton is composed. This structural model also explains the very efficient infrared opacification.[2,10] Theoretical calculations have reproduced the thermal conductivity behavior of our aerogels by assuming a partial coverage of the silica nanospheres. Silica spheres covered with a carbon layer of a few nanometer thickness provide the same very high mass specific extinction as solid carbon spheres.[2,3]

Increase of the Carbon Content by Treatment with Hydrocarbon Gases. The highest specific extinctions at 2–8 μm of pyrolyzed organically substituted aerogels are in the range of 200 m^2 kg^{-1}. A further increase by applying temperatures higher than 1000 °C or holding the samples at 1000 °C for a longer period of time (to generate more extended carbon structures) is not a good choice. Under these conditions significant sintering of the silica skeleton cannot be avoided, which would increase the density of the materials and thus the heat transport. An even more effective infrared opacification therefore is possible only by increasing the carbon content. The highest carbon content (14% for an aerogel with a density of 200–300 kg m^{-3}) was obtained by pyrolysis of **Ph20**. As discussed above, incorporation of a significantly higher percentage of organic groups would affect the nanostructure of the aerogels. Therefore, the only possibility of increasing the carbon content is from an external source. Our notion was that after pyrolysis of the organically substituted aerogels there would be enough carbon nuclei to facilitate pyrolysis of a hydrocarbon gas.

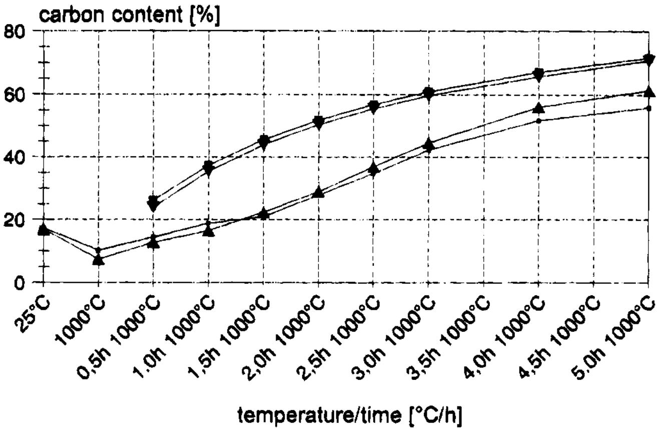

Figure 4. Carbon content (determined by elemental analysis) of pyrolyzed **Ph20** upon treatment with CH_4/Ar. Starting density 151 kg m^{-3}: (●) found; (■) maximum; starting density 87 kg m^{-3}: (▲) found, (▼) maximum.

When the "normal" pyrolysis process was finished, the samples were held at 1000 °C with a 1:1 mixture of CH_4 and Ar passing over them (CH_4 being representative for other hydrocarbons). The upper curves in Figure 4 give the amount of incorporated carbon if all the available CH_4 were pyrolyzed. The lower curves show the experimentally found carbon (aerogel **Ph20** with two different densities). About 50% of the available carbon is incorporated in the aerogels. After 5 h graphitic structures cover the outer surface of the samples, and the silica/carbon aerogel composites consist of about 60% carbon. Up to this point we could not detect a carbon gradient through the thickness of our cylindrical samples within the experimental error of limit. After formation of the graphitic layer at the outside of the samples, no further carbon was integrated *inside* the samples.

The comparison of both aerogels shows that more carbon is incorporated in the aerogel with the higher density at the beginning of the CH_4 treatment. However, carbon incorporation gets less efficient with time. This suggests that the higher initial carbon concentration in this aerogel catalyzes the CH_4 pyrolysis more efficiently at the beginning. When the pyrolysis process continues, the growth of the carbon structures is somewhat inhibited by the diffusion of CH_4. In the lower density aerogel, diffusion is of course less a problem, and therefore the carbon structures can grow more easily.

During the CH_4 treatment the specific extinction initially increases. In the 151 kg m^{-3} **Ph20** aerogel it increases by a factor of 5 to about 500 m^2 kg^{-1} at 5 μm within the first 2 h. Then it drops to about 300 m^2 kg^{-1} after 5 h. We interpret this result in a way that initially new carbon particles are formed by the CH_4 treatment or larger areas of the inner surface of the aerogel are covered with carbon. When the CH_4 treatment is continued, the carbon structures grow, and the extinc-

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(14) Tuinstra, F.; Koenig, J. I. *Chem. Phys.* **1970**, *53*, 1126.

tion is lowered due to scattering. In the 87 kg m^{-3} **Ph20** aerogel an even higher extinction of about 1000 m^2 kg^{-1} is reached after 3 h of CH_4 treatment. This is the highest extinction ever reached for a porous silica material.

Pyrolysis of CH_4 is obviously facilitated by the presence of carbon nuclei. We wanted to test whether the very active surface of silica aerogels alone is sufficient to generate carbonaceous structures from methane. Since the unmodified aerogel **00** contains residual OCH_3 groups as an "internal" source for carbon during pyrolysis, as discussed above, we used a commercially available aerogel (Basogel, BASF AG, approximate density of 200 kg m^{-3}, specific surface area 488 m^2 kg^{-1}) for comparison. This aerogel is made from water glass and therefore contains even less carbon (2.30% by elemental analysis).

The Basogel was heated to 1000 °C in the same way as the organically modified aerogels and then treated with CH_4/Ar. The general appearance of the carbon content vs. time curve is similar to that in Figure 4, but the similarity with an Avrami function is even more pronounced. However, the carbon incorporation within the first 2 h is rather low (about 5%). In this stage carbon nuclei are obviously formed. Then the rate of carbon formation rapidly increases. The aerogel contains about 30% carbon after 5 h and 45% carbon after 10 h of CH_4 treatment. The specific extinction of these silica/carbon composites is lower (400 m^2 kg^{-1}) than that of the CH_4-treated aerogels with carbon nuclei from pyrolyzed organic groups. Possible reasons may be a less effective coverage of the inner surface of the aerogel by the carbon structure or a different size of the primary particles in Basogel (which was not determined).

Conclusions

We have shown that controlled pyrolysis of organically substituted silica aerogels is a very effective method of generating carbonaceous structures for infrared opacification. Specific extinction can be substantially increased by subsequent treatment with CH_4 at 1000 °C, up to about 1000 m^2 kg^{-1}. Compared with conventional methods, this method results in a higher specific extinction at a given carbon content due to the very effective coverage of the inner surface of the aerogels. By the CH_4 treatment the carbon content can be increased beyond a point not possible with other methods. Most important, the aerogel structure is basically maintained during the pyrolysis process. The development of the carbonaceous structures and the structural changes of the aerogel during pyrolysis depend to a very high degree on the kind of organic groups initially present in the aerogels. Therefore, the careful optimization of the process is necessary.

Experimental Section

Preparation of the Organically Modified Aerogels. "Alcogels" were prepared by hydrolysis and co-condensation of methanolic solutions of tetramethoxysilane (TMOS) and an organically substituted trialkoxysilane $RSi(OMe)_3$ (R = methyl, phenyl, vinyl, propyl) as described in ref 4a,b. The alkoxysilanes were used as received (ABCR, Fluka, purity 97–99%). For the preparation of the aerogels **Me20**, **Vi20**, **Ph20**, and **Pr20**, a 4:1 ratio of $Si(OMe)_4$ and $RSi(OMe)_3$ was employed, and a 3:2 ratio for **Me40**. The gels were prepared under basic conditions by adding a calculated amount of 0.01 N aqueous NH_4OH, corresponding to the amount of water necessary to hydrolyze all SiOMe groups. The solution was stirred for 5–10 min. The density of the alcogel was adjusted by adding an appropriate amount of methanol to the mixtures of alkoxy silanes. After gelation, the samples were aged for 7 days at 30 °C in closed polyethylene vessels. The supercritical drying process was then carried out with methanol. The temperature was increased to 270 °C during 8 h, while the pressure increased to 120 bar. After 3 h in the supercritical state, the methanol was removed during 6 h. Cylindrical aerogels were obtained. The process was computer controlled to get a good reproducibility.

Pyrolysis of the Organically Modified Aerogels. Aerogel pieces or slices (2.1 cm diameter, 3–10 mm thick) were placed in a quartz boat located in the center of a horizontal quartz tube (2.5 cm diameter, 50 cm length), equipped with a pressure-release bubbler at one end and a gas inlet at the other end. The quartz tube was electrically heated to 400 °C (10 °C/min) while being flushed with a slight stream of argon. Above 400 °C flushing with Ar was discontinued and the temperature raised to 1000 °C with a rate of 1 °C/min.

Increase of the carbon content was achieved by holding the samples at 1000 °C, with a 1:1 mixture of CH_4 and Ar passing through the tube (200 cm^3/min).

Characterization. The composition of the aerogels was determined by elemental analyses. The shrinkage during supercritical drying was determined by measuring the diameter of the cylindrical sample before and after supercritical drying. The density was calculated from the mass and the volume of the cylindrical samples. The specific surface areas and pore radii distributions were determined by the BET method (Micromeritics Sorptomat ASAP 2400).

Small-angle X-ray scattering experiments (SAXS) were performed on selected samples using the beamline JUSIFA at HASYLAB/Hamburg (Germany).

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