

# Time-Efficient Acid-Catalyzed Synthesis of Resorcinol–Formaldehyde Aerogels

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Resorcinol (R)–formaldehyde (F) aerogels are pursued as precursors of carbon aerogels, which are electrically conducting. They are usually prepared via a week-long base-catalyzed gelation process from an aqueous sol. For this work, we reasoned that because both the reaction of R with F and the condensation of the resulting hydroxymethyl resorcinol with R are electrophilic aromatic substitutions, they should proceed easily by acid catalysis in one pot. Thereby, we have developed and reported an HCl-catalyzed gelation process in CH<sub>3</sub>CN, which is completed in about 2 h at room temperature or in 10 min at 80 °C. The final aerogels are chemically indistinguishable (by IR and <sup>13</sup>C CPMAS NMR) from typical base-catalyzed samples. In analogy to phenol–formaldehyde resin formation, the mechanism may involve *o*-quinone methide intermediates (hence the red color prevailing throughout the process). The effect of aging is discussed in terms of shrinkage and is attributed to further reaction and incorporation of more formaldehyde into wet gels, followed by syneresis (reaction with one another of dangling oligomeric appendices on the skeletal framework).

## 1. Introduction

Aerogels comprise a special class of low-density open cell foams with large internal void space, which is responsible for useful materials properties such as low thermal conductivity, high surface area, and high acoustic impedance.<sup>1</sup> Chemically, most aerogels consist of inorganic networks of metal and semimetal oxide nanoparticles, usually silica. On the other hand, resorcinol–formaldehyde (RF) aerogels are the most well-known organic aerogels and are pursued not only for their typical aerogel properties, but also most importantly as precursors to electrically conducting carbon aerogels.<sup>2</sup> Typically, RF aerogels are prepared via Pekala's method that involves base (Na<sub>2</sub>CO<sub>3</sub>)-catalyzed gelation of aqueous solutions of resorcinol with formaldehyde, followed by aging and drying from supercritical fluid (SCF) CO<sub>2</sub>.<sup>3–6</sup> RF aerogels exhibit high porosity (>80%), high surface area (>400 m<sup>2</sup>g<sup>-1</sup>), ultrafine cell size (<500 Å), and densities as low as 0.03 g cm<sup>-3</sup>. Mechanistically, the role of the base catalyst has been explained in terms of deprotonation of the OH group of resorcinol to O<sup>-</sup>, which is a strong electron donor and thus an effective activator of the aromatic ring toward electrophilic aromatic hydroxymethylation via reaction with formaldehyde. In turn, formation of hydroxymethyl derivatives of resorcinol is followed by condensation to methylene (CH<sub>2</sub>) and methylene ether (CH<sub>2</sub>–O–CH<sub>2</sub>) bridges. Within the context of this mechanism, the effect of the

preparation conditions on the aerogel nanostructure has been studied extensively. The R:C mol ratio is typically varied in the 50–300 range. For high resorcinol-to-catalyst ratio (e.g., R:C ≈ 1 500) formation of interconnected microspheres has been reported.<sup>7,8</sup> Smaller particles connected with large necks were observed with low R:C ratios (e.g., 50).<sup>9</sup> The final pore structure depends strongly on the sol pH.<sup>10</sup> The major drawback of the base-catalyzed method seems to be the long gelation time, which typically extends up to 7 days at 85 °C and is followed by aging for at least another 3 days in CF<sub>3</sub>COOH at 45 °C.

The extensive literature on base-catalyzed RF aerogels overshadows the few reports on acid-catalyzed processes. Those include gelation in HClO<sub>4</sub>/acetone at 45 °C followed by 3 days of aging,<sup>11</sup> in aqueous HNO<sub>3</sub> at 80 °C (2 day gelation, 7 days aging),<sup>12</sup> and in acetic acid at room temperature (1 day gelation, 3 days of aging at 50 °C, and 3 days at 90 °C).<sup>13</sup> The general observation is that processes involving acid catalysis are shorter. In that regard, the shortest process we are aware of is a hybrid method in which resorcinol and propanal are first incubated with triethylamine (Et<sub>3</sub>N) in CH<sub>3</sub>CN for 1 h at 80 °C, followed by addition of

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HCl and room-temperature gelation within 1–2 min.<sup>14</sup> However, when we attempted the same process for the synthesis of RF gels, addition of HCl at the prescribed amounts caused precipitation of triethylammonium chloride, contaminating the gels. At that point we questioned the need for Et<sub>3</sub>N, and more generally the effectiveness of the base-catalyzed route: our reasoning was that on the one hand, O<sup>-</sup> is a better electron donor than OH, but not very much so ( $\sigma_{p,O^-} = -0.81$  vs  $\sigma_{p,OH} = -0.37$ ).<sup>15</sup> On the other hand, addition of formaldehyde is an electrophilic aromatic substitution reaction, and as such it should be accelerated by acid catalysis. In fact, chloromethylation of aromatic systems (i.e., addition of CH<sub>2</sub>Cl) using stoichiometric amounts of formaldehyde and HCl is an efficient and well-known reaction.<sup>16a</sup> By using only a catalytic amount of HCl, the reaction should proceed as hydroxymethylation (Lederer–Manasse reaction),<sup>16b</sup> adding the same functionality (CH<sub>2</sub>OH) as the base-catalyzed route. Furthermore, acid catalysis should also promote in one pot a subsequent condensation step by protonation of the newly formed CH<sub>2</sub>OH groups leading to Bakelite-type resins.<sup>16b</sup> On the basis of this line of reasoning, we have developed and described here an HCl-catalyzed gelation process that is completed in minutes rather than days, yielding gels indistinguishable from those obtained by the usual base-catalyzed process in a week. Importantly, RF gels processed with no aging at all shrink significantly less and therefore are lower density materials than gels aged for a few days.

## 2. Experimental Section

**Materials.** Formaldehyde (37% w/w aqueous solution methanol stabilized) and acetone (anhydrous) were used as received from Aldrich Chemical Co. Acetonitrile (ACS reagent grade) and hydrochloric acid (12.1 N) were purchased from Fisher Scientific. Syphon grade CO<sub>2</sub> was obtained from BOC Gases, Murray Hill, N.J., supplied locally by Ozarc Gases.

HCl-catalyzed RF gels were prepared using resorcinol (R) and formaldehyde (F) in four different R:F mol ratios (1:2, 1:3, 1:5, and 1:10; sols made with R:F = 1:20 did not gel). For example, RF gels with a 1:2 mol ratio were prepared by mixing two solutions at room temperature: solution “A” containing 0.337 g (3.06 mmol) of resorcinol, 0.477 mL (6.29 mmol) of the commercially available formaldehyde solution, and 11.5 mL CH<sub>3</sub>CN; and solution “B” containing 0.636 mL of CH<sub>3</sub>CN and 0.03 mL (0.363 mmol) of concentrated (12.1 N) HCl (R:C = 8.4). The mixture (sol) was poured into polypropylene molds (Wheaton polypropylene Omni-Vials, part 225402, ~1 cm in diameter) and gelled within 2 h at room temperature or in about 10 min at 80 °C. Although it might not be an advantage, typically, the resulting gels were aged in their molds at room temperature for 24 h and subsequently washed with acetone (3×, 8 h, 20 mL of acetone each time) and dried in an autoclave with liquid CO<sub>2</sub>. Thus, liquid CO<sub>2</sub> at 14 °C first extracts the pore-filling solvent (acetone with traces of CH<sub>3</sub>CN) out of the wet gels, and when there is no more solvent coming out of the

gels, the temperature and pressure of the autoclave are taken above the critical point of CO<sub>2</sub> (32 °C, 73.8 bar), which is then vented off isothermally at 40 °C.

For comparison, Na<sub>2</sub>CO<sub>3</sub>-catalyzed RF gels were made from an aqueous solution at 85 °C according to Pekala’s method using R:F and R:C ratios equal to 1:2 and 72.5, respectively (200 mL of H<sub>2</sub>O, 6.39 g of R (0.29 M), 8.64 mL of the 37% aq. solution of F (0.57 M), and 0.23 g of Na<sub>2</sub>CO<sub>3</sub>).<sup>3</sup> Gelation took place in 7 days. Although gels were aged for 3 additional days in a 0.125% w/w CF<sub>3</sub>COOH in H<sub>2</sub>O at 45 °C in Pekala’s method, for our purposes here, some gels were aged for 3 days in their original molds for comparison. At the end, all gels, either aged in their original molds or in aqueous CF<sub>3</sub>COOH, were solvent-exchanged with acetone (4 washes, 8 h each time) and dried with CO<sub>2</sub> taken supercritically. Gels aged in their molds swell to about double their size in acetone; they are also extremely fragile and do not survive the transfer to the autoclave in one piece. Na<sub>2</sub>CO<sub>3</sub>-catalyzed gels aged in CF<sub>3</sub>COOH are much sturdier and behave like the 10 min HCl gels of this study.

**Methods.** The early stages of the reaction between resorcinol and formaldehyde were investigated by (a) recording <sup>13</sup>C NMR spectra under various conditions using a 400 MHz Varian Unity Inova NMR instrument; (b) carrying out the reaction in a UV cuvette placed in a Beckman DU 640B UV-vis spectrophotometer; and (c) monitoring the viscosity of the sol according to ASTM Designation D 562-01 “Standard Test Method for Consistency of Paints Measuring Krebs Unit (KU) Viscosity Using a Stormer Type Viscometer.” Supercritical fluid CO<sub>2</sub> drying was conducted using an autoclave (SPI-DRY Jumbo Supercritical Point Drier, SPI Supplies, Inc., West Chester, PA). Chemical characterization of RF aerogels was conducted with infrared and <sup>13</sup>C NMR spectroscopies. Infrared spectra were obtained in KBr pellets using a Nicolet-FTIR model 750 spectrometer. Solid <sup>13</sup>C NMR spectra were obtained with samples ground in fine powders on a Bruker Avance 300 Spectrometer with 75.475 MHz carbon frequency using magic angle spinning (7 kHz) with broadband proton suppression and the CPSELTICS pulse sequence for spin sideband suppression. Spectra were externally referenced to the carbonyl of glycine (196.1 ppm relative to tetramethylsilane). Bulk densities were calculated from the weight and physical dimensions of the samples. Skeletal densities were determined by helium pycnometry using Micromeritics AccuPyc 1330 instruments. Mesoporous surface areas and pore size distributions were measured by nitrogen adsorption/desorption porosimetry using a Micromeritics ASAP 2000 surface area/pore distribution analyzer. Samples for surface area and skeletal density determination were outgassed at 80 °C for 24 h before analysis. Scanning electron microscopy was conducted with samples coated with Au using a Hitachi S-4700 field emission microscope.

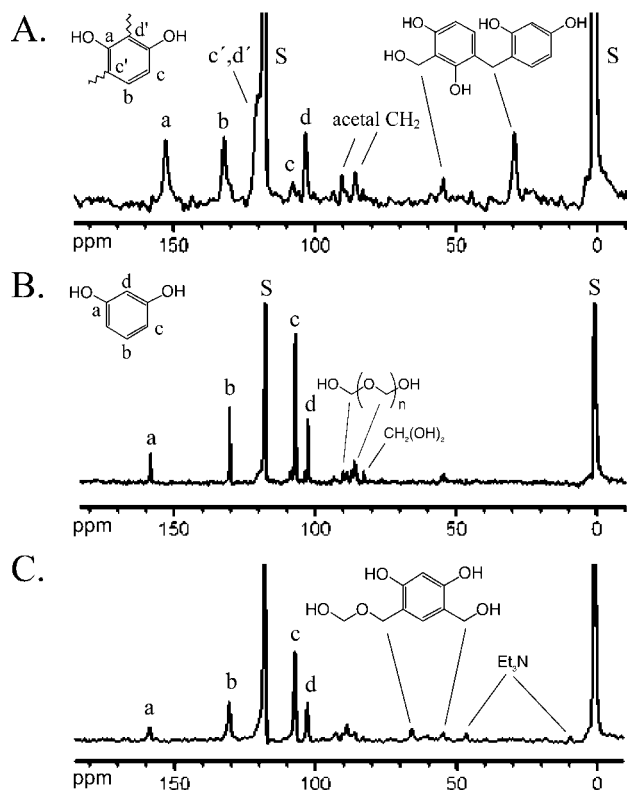
## 3. Results

**(a) Reaction of Resorcinol with Formaldehyde in HCl-Catalyzed CH<sub>3</sub>CN Solutions.** On the basis of our working hypothesis, namely that both electrophilic aromatic hydroxymethylation and the subsequent condensation of the resulting aromatic systems should both be favored by acid catalysis, it was first decided to compare the reaction of resorcinol with formaldehyde in acetonitrile with an acid catalyst (HCl), a base catalyst (Et<sub>3</sub>N), and with no catalyst at all. The progress of the reaction was monitored with <sup>13</sup>C NMR in CD<sub>3</sub>CN 15 min after mixing R with F using a 1:2

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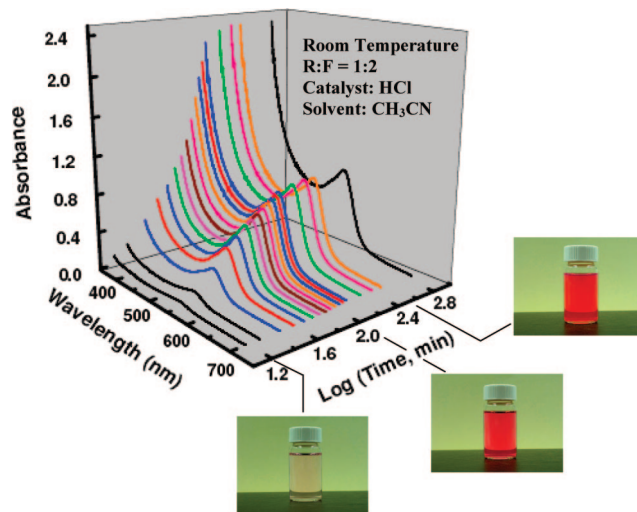
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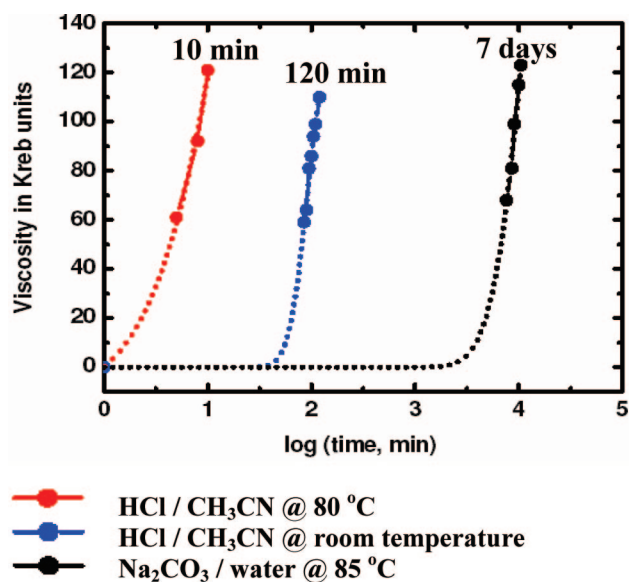


**Figure 1.** Solution  $^{13}\text{C}$  NMR of a 1:2 (mol/mol) resorcinol:formaldehyde mixture in in  $\text{CD}_3\text{CN}$ : (A) 15 min after mixing, using HCl as catalyst, at room temperature; (B) 15 min after mixing, without any catalyst, at room temperature; and (C) 75 min after mixing, with  $\text{Et}_3\text{N}$  as catalyst, at  $80^\circ\text{C}$  (S, solvent).

R:F molar ratio (Figure 1). Peak assignment was based on Werstler's analysis<sup>17</sup> and our own spectra simulations. By comparing panels A and B in Figure 1 (HCl-catalyzed vs noncatalyzed reaction, respectively), we see clearly that the position of the phenolic carbon has been shifted upfield (152.8 ppm, Figure 1A) relative to the noncatalyzed solution (158.5 ppm, Figure 1B), and the carbon in the meta position relative to both phenols (carbon b) has been shifted slightly downfield (to 132.2 ppm from 130.6 ppm). The intensity of the aromatic carbons of resorcinol designated as c and d at 107.5 and 102.7 ppm, respectively (Figure 1B), has been decreased and a new peak partially merging with acetonitrile has appeared at  $\sim 120$  ppm (Figure 1A). The peak at  $\sim 83.1$  ppm, present in both reaction mixtures, is assigned to methylene glycol from formaldehyde, whereas peaks in the 85–86 ppm range are attributed to condensation products of formaldehyde (e.g.,  $\text{O}-\text{CH}_2-\text{O}-\text{CH}_2-\text{O}-$ ). Both reaction mixtures (panels A and B in Figure 1) show small peaks at 54.5 ppm corresponding to aromatic  $\text{CH}_2\text{OH}$  carbons, but the spectrum of the HCl-catalyzed mixture (Figure 1A) is dominated by the peak at 29.5 ppm, which is assigned to  $\text{CH}_2$  carbons sandwiched between two aromatic rings. Certainly, this resonance supports fast condensation of hydroxymethylated resorcinol with resorcinol and is completely absent from the spectrum of the noncatalyzed reaction mixture. Similarly to the noncatalyzed mixture of Figure 1B, base-catalyzed reactions kept at room temperature show a



**Figure 2.** Evolution of the absorbance of a 1:2 (mol/mol) resorcinol:formaldehyde mixture in  $\text{CH}_3\text{CN}$  at room temperature. Pictures show snapshots of the red color at specified points in time.



**Figure 3.** Viscosity evolution of three solutions as indicated, according to ASTM D 562–01. The Stormer type Viscometer employed was able to register data only above 59 Krebs units. Data collection stopped at the gel point.

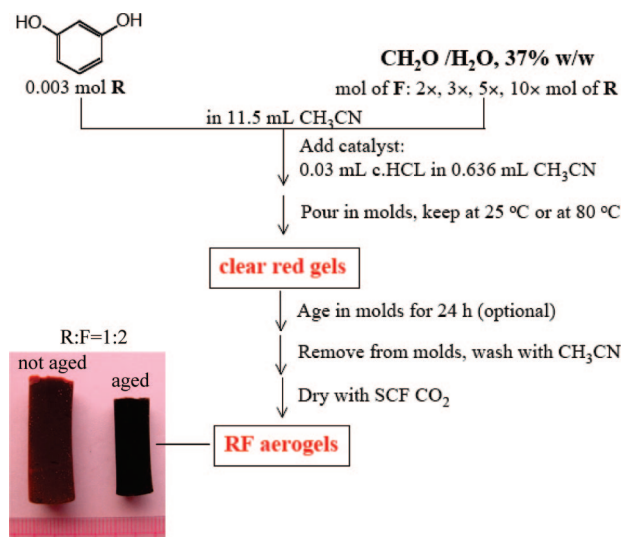
small peak at 54.5 ppm assigned to aromatic  $\text{CH}_2\text{OH}$  (data not shown), and if heated at  $80^\circ\text{C}$ , they show an additional new resonance at 66.0 ppm (Figure 1C) assigned to aromatic  $\text{CH}_2-\text{O}-\text{CH}_2\text{OH}$ . No signals of bridging  $\text{CH}_2$  groups at  $\sim 30$  ppm are visible. Overall,  $^{13}\text{C}$  NMR data confirm that the RF reaction proceeds faster under HCl-catalyzed conditions. But, is this faster reaction rate of any practical consequence?

HCl-catalyzed RF solutions in  $\text{CH}_3\text{CN}$  quickly develop a characteristic red color ( $\lambda_{\text{max}}=543$  nm, Figure 2) and gel. Gelation was followed by viscosity measurements with a Stormer-type paddle viscometer both at room temperature and at  $80^\circ\text{C}$ . As shown in Figure 3, HCl-catalyzed RF solutions in  $\text{CH}_3\text{CN}$  gel within 2 h at room temperature and within 10 min at  $80^\circ\text{C}$ . By comparison, noncatalyzed or  $\text{Et}_3\text{N}$ -catalyzed mixtures do not gel at  $80^\circ\text{C}$  in at least a day. The aqueous  $\text{Na}_2\text{CO}_3$ -catalyzed sol kept at  $85^\circ\text{C}$  gels in 7 days, consistent with the literature.<sup>3</sup>

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### Scheme 1. Time-Efficient Synthesis of Resorcinol-Formaldehyde Aerogels



#### (b) Time-Efficient Preparation and Characterization of RF Aerogels.

The qualitative findings of Section 3a were formalized as shown in Scheme 1. The absolute amounts of R and catalyst (see Experimental Section) were chosen to match those of the Baumann's Et<sub>3</sub>N/HCl method of gelation of R with propanal.<sup>14</sup> The R:F mol ratio was varied from 1:2 to 1:10. Wet gels made with 1:2, 1:3, and 1:5 R:F molar ratios are red and clear; gels prepared with a 1:10 R:F molar ratio are pink and opaque. In general, wet gels were aged in their molds for 24 h; they were then removed, washed with acetone, and dried with liquid CO<sub>2</sub> taken out supercritically. Appearance-wise, HCl-catalyzed RF gels made within 10 min in CH<sub>3</sub>CN using a 1:2 R:F molar ratio as shown in Scheme 1 are pretty similar to samples made through the week-long process in aqueous Na<sub>2</sub>CO<sub>3</sub>. All samples were characterized for shrinkage by comparing their physical dimensions relative to their mold (whenever possible). All pertinent physical characterization data are summarized in Table 1. Because HCl-catalyzed sols gel in only 10 min at 80 °C, a subsequent long aging period creates an asymmetry in the whole process and is not practical. For this, representative R:F = 1:2 gels were also processed without aging and relevant data are included in Table 1.

Although wet gels made with the HCl-catalyzed process do not seem to shrink relative to the molds, RF aerogels do shrink relative to their wet gels upon drying with SCF CO<sub>2</sub>. The shrinkage is not related to the R:F ratio, but it does depend on the aging time. Gels processed with no aging at all shrink less (~29%), whereas gels aged for a prolonged period (1–5 days) shrink more (~39%). Shrinkage is reflected on the bulk density, which is found lowest for samples processed with no aging at all. Skeletal densities are about equal to one another for the different R:F ratios, and porosity (% empty space), Π, calculated from the bulk and skeletal densities (ρ<sub>b</sub> and ρ<sub>s</sub>, respectively) via Π = 100 × [(1/ρ<sub>b</sub>) - (1/ρ<sub>s</sub>)]/(1/ρ<sub>b</sub>) is in the 87–93% range. RF aerogels with the lowest bulk density (those processed with no aging at all) are the ones with the highest porosity. For comparison purposes, Table 1 also includes data for Na<sub>2</sub>CO<sub>3</sub>-catalyzed gels made here by adhering closely to Pekala's procedure.<sup>3</sup>

It is noted that such aerogels produced without the prescribed 3 day aging in CF<sub>3</sub>COOH do not have the strength required to yield monoliths. On the other hand, gels that have gone through the CF<sub>3</sub>COOH aging process show similar processability to those made by the HCl-catalyzed process in CH<sub>3</sub>CN.

Microscopically, HCl-catalyzed RF aerogels consist of a beadlike structure, pretty similar to both the structure of base-catalyzed RF aerogels<sup>18</sup> and the typical pearl-necklace-like structure of common base-catalyzed mesoporous silica.<sup>19,20</sup> Figure 4 compares the SEMs of a HCl-catalyzed RF aerogel and a base-catalyzed silica aerogel. In agreement with SEM, N<sub>2</sub> sorption porosimetry yields characteristic type IV isotherms for mesoporous materials (Figure 5). The average pore size was calculated by the 4V<sub>total</sub>/σ method, using values for V<sub>total</sub> calculated by two methods: via a single point measurement of the volume of N<sub>2</sub> adsorbed, and via the bulk and skeletal densities (ρ<sub>b</sub> and ρ<sub>s</sub>, respectively, see footnote g in Table 1). The single point N<sub>2</sub> adsorption method tends to underestimate V<sub>total</sub> significantly,<sup>21</sup> but average pore sizes calculated by that method are still included here for comparison with previously reported data for other kinds of aerogels. Thus, the average pore size by the N<sub>2</sub> adsorption method is in the same range (12–23 nm) as for base-catalyzed mesoporous silica aerogels.<sup>20</sup> From Table 1, there is a clear correlation between average pore size, bulk density, and porosity: the lower the bulk density, the higher the porosity and the larger the average pore sizes. By the same token, however, specific surface areas, σ, of our HCl-catalyzed RF aerogels measured by the BET method are lower than those of the corresponding base-catalyzed not only RF but also silica aerogels of similar density and pore sizes: 300–500 m<sup>2</sup> g<sup>-1</sup> for HCl-catalyzed RF aerogels versus 700–800 m<sup>2</sup> g<sup>-1</sup> for Na<sub>2</sub>CO<sub>3</sub>-catalyzed RF aerogels (Table 1) and ~1000 m<sup>2</sup> g<sup>-1</sup> for base-catalyzed silica aerogels.<sup>20b</sup> From the specific BET surface area, σ, and skeletal density, ρ<sub>s</sub>, we can calculate the average particle radius r (= 3/ρ<sub>s</sub>σ).<sup>22</sup> The particle diameters (=2r) are included in Table 1, and there is a good agreement with the particle sizes observed with SEM and with the particle sizes both calculated (Table 1) and reported for typical base-catalyzed RF aerogels.<sup>3</sup>

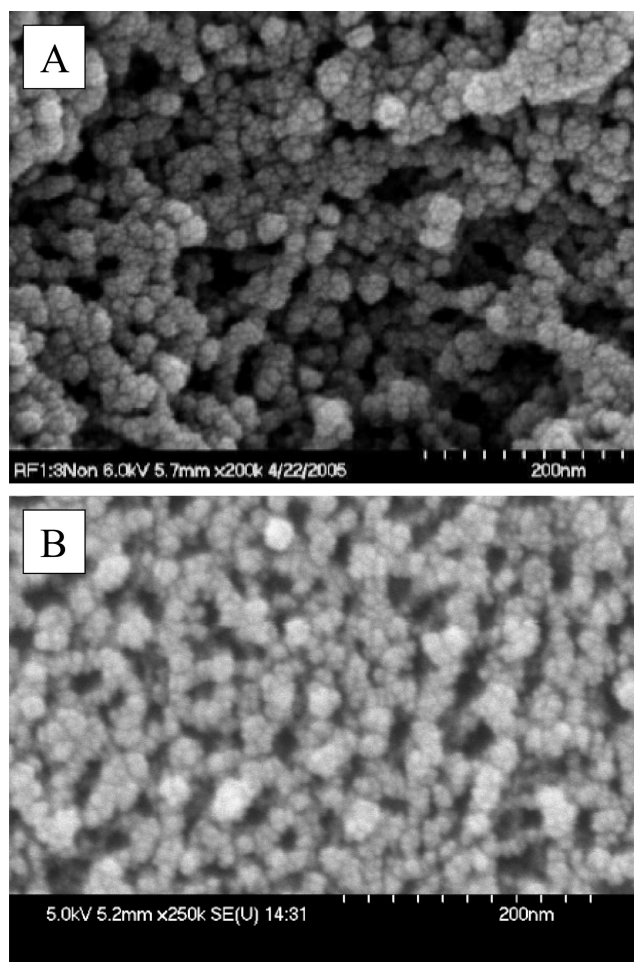
The chemical make up of our HCl-catalyzed RF aerogels was investigated with IR and <sup>13</sup>C NMR. The IR spectrum of a typical RF aerogel (Figure 6) shows the same features to those shown by Na<sub>2</sub>CO<sub>3</sub>-catalyzed aerogels,<sup>3</sup> with bands at 2942, 2842, and 1479 cm<sup>-1</sup> associated with the CH<sub>2</sub> stretching and bending vibrations, whereas the broadband at 3382 cm<sup>-1</sup> includes the aromatic OH groups of resorcinol.

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**Table 1. Physical Characterization Data for RF Aerogels Processed under Various Conditions**

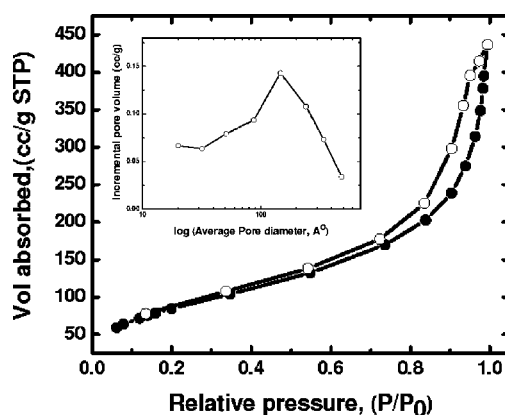
R:F	aging Time (days)	diameter (cm)	% shrinkage <sup>f</sup>	bulk density (g cm <sup>-3</sup> )	skeletal density (g cm <sup>-3</sup> )	porosity (% void space)	BET surface area [avg pore diameter <sup>g</sup> ] (m <sup>2</sup> g <sup>-1</sup> [nm])	particle diameter (nm) <sup>h</sup>
via HCl-Catalyzed Gels in CH <sub>3</sub> CN								
1:2 <sup>a</sup>	0 <sup>i</sup>	0.94 ± 0.02 <sup>c</sup>	29	0.101 ± 0.007	1.492 ± 0.006 <sup>e</sup>	93.2 ± 0.9	314 [22.9; 118]	12.8
1:2 <sup>b</sup>	1 <sup>j</sup>	0.65 ± 0.02 <sup>d</sup>	38	0.136 ± 0.008	1.363 ± 0.056	90.0 ± 0.8	318 [14.7; 83.3]	13.8
1:2 <sup>a</sup>	5 <sup>j</sup>	0.81 ± 0.01 <sup>c</sup>	39	0.157 ± 0.004	1.459 ± 0.002 <sup>e</sup>	89.2 ± 0.9	512 [12.6; 44.4]	8.03
1:3 <sup>b</sup>	1 <sup>j</sup>	0.63 ± 0.02 <sup>d</sup>	39	0.175 ± 0.008	1.386 ± 0.030	87.4 ± 0.4	437 [15.0; 45.6]	9.91
1:5 <sup>b</sup>	1 <sup>j</sup>	0.63 ± 0.01 <sup>d</sup>	39	0.159 ± 0.005	1.368 ± 0.021	88.4 ± 0.2	363 [14.6; 61.2]	12.0
1:10 <sup>b</sup>	1 <sup>j</sup>	0.63 ± 0.001 <sup>d</sup>	39	0.164 ± 0.010	1.565	90.2 ± 0.2	351 [10.8; 51.7]	10.9
via Na <sub>2</sub> CO <sub>3</sub> -Catalyzed Gels in Water <sup>3</sup>								
1:2 <sup>i</sup>	3 <sup>j</sup>	<sup>l</sup>	<sup>l</sup>	<sup>l</sup>	1.481 ± 0.004	<sup>l</sup>	818 [19.4]	4.95
1:2 <sup>i</sup>	3 <sup>k</sup>	1.52 ± 0.04 <sup>m</sup>	40	0.173 ± 0.006	1.458 ± 0.006	88.1 ± 0.5	744 [15.3; 27.4]	5.53

<sup>a</sup> Average of 5 samples. <sup>b</sup> Average of 3 samples. <sup>c</sup> Made in 1.33 cm diameter cylindrical molds. <sup>d</sup> Made in 1.04 cm diameter cylindrical molds. <sup>e</sup> Those skeletal densities were determined on a different instrument at a different time. <sup>f</sup> All shrinkage is observed after drying with SCF CO<sub>2</sub>. Gels do not show shrinkage relative to the molds. <sup>g</sup> By the  $4V_{\text{total}}/\sigma$  method (where  $V_{\text{total}}$  = mass specific total pore volume,  $\sigma$  = mass specific surface area by the BET method).  $V_{\text{total}}$  has been calculated by two methods, hence the two numbers cited for the average pore diameter: first automatically by the system software from single point volume measurements of N<sub>2</sub> adsorbed (from the N<sub>2</sub> adsorption curves, e.g., see Figure 5), and second, manually from the bulk and skeletal densities via  $V_{\text{total}} = (1/\rho_b) - (1/\rho_s)$ , where  $\rho_b$  and  $\rho_s$  represent the bulk and skeletal densities, respectively). <sup>h</sup> Diameter = 2r, where  $r = 3/\sigma\rho_s$  ( $r$  = particle radius). <sup>i</sup> Average of 2 samples. <sup>j</sup> Aged in the molds. <sup>k</sup> Aged in aqueous CF<sub>3</sub>COOH (see Experimental Section). <sup>l</sup> Gel is too fragile; it does not survive transfer to the autoclave. <sup>m</sup> Made in 2.50 cm diameter cylindrical molds.

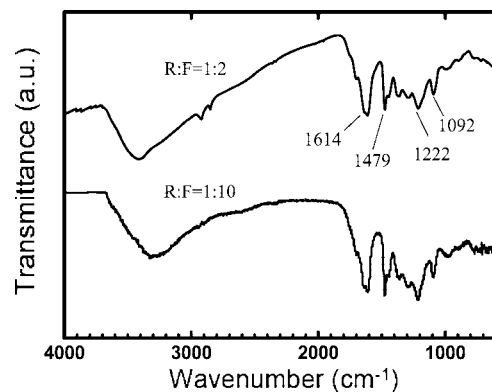


**Figure 4.** (A) SEM of a RF aerogel (bulk density  $\rho_b = 0.175 \pm 0.008$  g cm<sup>-3</sup>) prepared according to Scheme 1, using a 1:3 R:F molar ratio. (B) For comparison, SEM of a native silica aerogel of similar density ( $\rho_b = 0.169 \pm 0.004$  g cm<sup>-3</sup>).<sup>20b</sup>

The band at 1614 cm<sup>-1</sup> comes from aromatic ring stretches, whereas medium to weak absorption bands at 1222 and 1092 cm<sup>-1</sup> indicate that methylene ether linkages between resorcinol rings are present but not dominant. Figure 7 compares the CPMAS <sup>13</sup>C NMR spectra of the two

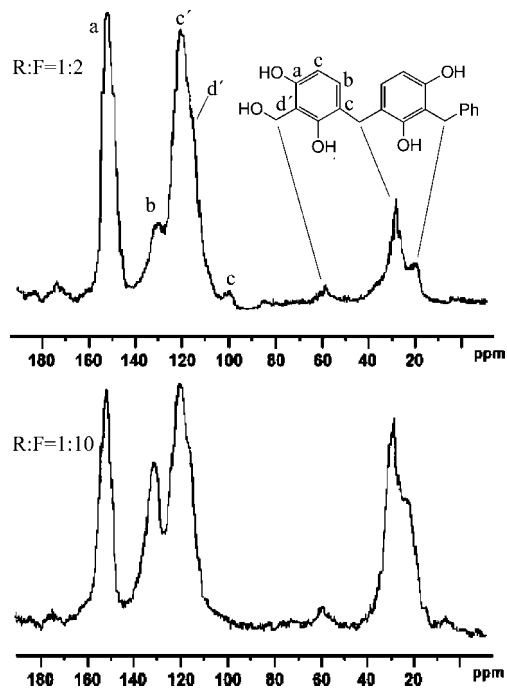


**Figure 5.** Nitrogen sorption isotherms for a RF aerogel prepared according to Scheme 1 using 1:2 R:F at room temperature, 1 day of aging ( $\rho_b = 0.136 \pm 0.008$  g cm<sup>-3</sup>). Adsorption, ●; desorption, ○. Inset: BJH desorption pore size distribution. Results in good agreement with the  $4V_{\text{total}}/\sigma$  by BET method, where  $V_{\text{total}}$  was calculated via the single point volume measurement of N<sub>2</sub> adsorption method (Table 1).



**Figure 6.** Infrared spectra (in KBr) of two RF aerogels prepared with the R:F ratios indicated.

extreme compositions of this study, one made with a 1:2 R:F molar ratio and another one with 1:10 R:F. Peak assignment was based on Figure 1 and ref 23. The resonance at 152 ppm is assigned to phenolic carbons of substituted resorcinol. On the other hand, RF aerogels may include aromatic rings with one, two, and three bridges



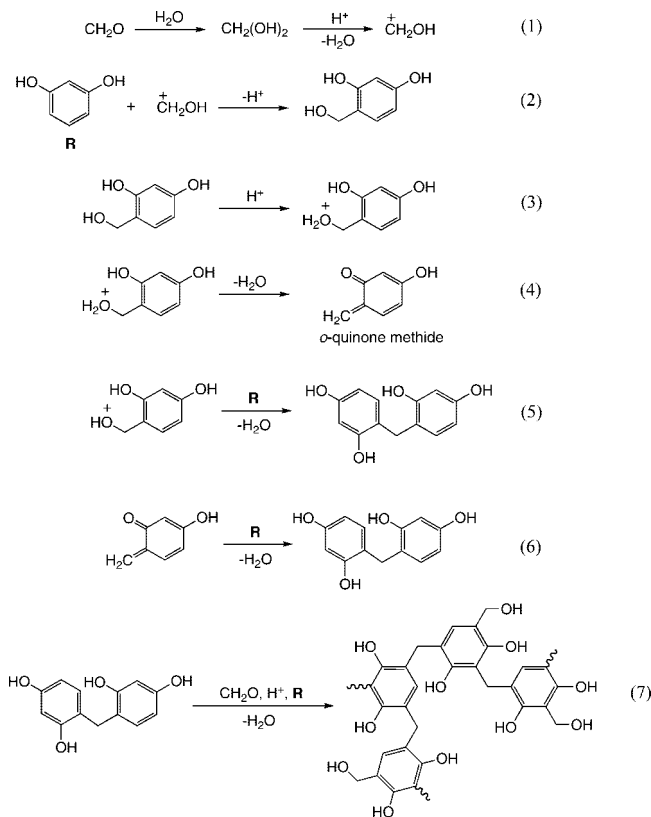
**Figure 7.**  $^{13}\text{C}$  CPMAS NMR of two RF aerogels as indicated. A higher content of formaldehyde in the sol results in more  $\text{CH}_2$  bridges. Relative integration of the resonances at 152 and 30 ppm indicates that gels prepared with a 1:10 R:F ratio incorporate 2.5 times more bridging  $\text{CH}_2$  than gels prepared with a 1:2 R:F ratio.

to adjacent rings, giving rise to broad asymmetric resonances. Thus, the peak at 121 ppm with a shoulder at 114 ppm is assigned to aromatic carbons of mono- and disubstituted resorcinols bearing  $\text{CH}_2$  groups in all ortho positions relative to the phenolic OHs ( $c'$ ,  $d'$ -carbons). Consistent with the IR spectrum, the smaller peak at 59 ppm is assigned to the small amount of  $\text{CH}_2\text{-O-CH}_2$  bridges that apparently decreases as the relative amount of formaldehyde is increased. The broad peak at 30 ppm with shoulder at 24 ppm is assigned to the different types of  $\text{CH}_2$  bridges. As the relative amount of formaldehyde is increased, the intensity of the bridging  $\text{CH}_2$  carbon increases, indicating incorporation of more formaldehyde into the gel. Integration of the aromatic phenolic carbon peak at 152 ppm vs the broad peak at 20–40 ppm shows incorporation of  $2.5\times$  more formaldehyde per aromatic ring in gels made with a 1:10 R:F molar ratio than in gels made with 1:2 R:F. Overall, the spectra of both kinds of aerogels (i.e., those made with 1:2 and 1:10 R:F) are qualitatively similar to those reported for the  $\text{Na}_2\text{CO}_3$ -catalyzed RF aerogels at high resorcinol-to-catalyst ratios (R:C = 200 and 500),<sup>23</sup> indicating a similar distribution of substitution sites.

#### 4. Discussion

In contrast to the base-catalyzed route to RF aerogels, which is based on activation of the aromatic ring toward electrophilic aromatic substitution by increasing the electron

#### Scheme 2. Proposed Mechanism for RF Gel Formation under Acid (HCl) Catalysis



donating ability of the substituents (from OH to  $\text{O}^-$ ), the acid-catalyzed route is based on acceleration of the reaction by increasing the positive charge of the electrophile. Comparative data shown in Figures 1 and 3 support this hypothesis: in the same solvent system ( $\text{CH}_3\text{CN}$ ), HCl-catalyzed R/F mixtures react and/or gel much faster than non- or base-catalyzed mixtures with a given reactant concentration. But the choice of solvent is also important: for example, running the same HCl-catalyzed process in acetone rather than in  $\text{CH}_3\text{CN}$ , leads to much slower gelation, presumably because of cross-aldol condensation type of equilibria between the solvent (acetone) and formaldehyde. Scheme 2 summarizes the proposed mechanism for the HCl-catalyzed gelation of resorcinol with formaldehyde. Protonation of formaldehyde (eq 1) is followed by nucleophilic attack by the  $\pi$ -system of resorcinol (eq 2) leading to hydroxymethylation. Subsequently, protonation of a hydroxymethyl group (eq 3) forms  $\text{OH}_2^+$ , a good leaving group, that may cleave either unimolecularly (eq 4), leading to  $o$ -quinone methide-type intermediates (also referred to as  $o$ -quinomethanes), or bimolecularly (eq 5) after direct attack at the  $\text{CH}_2\text{OH}_2^+$  carbon by the  $\pi$ -system of another resorcinol molecule. The latter process results directly into  $\text{CH}_2$  bridge formation between phenyl rings at three possible positions. On the other hand,  $o$ -quinone methides are quite unstable species, having been observed only as transients during pulse radiolysis experiments,<sup>24</sup> or in solid argon matrices.<sup>25</sup> At higher temperatures (e.g.,  $\sim -30^\circ\text{C}$ )  $o$ -quinone

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methides start Diels–Alder reactions with one another and form spiro dimers and trimers.<sup>25b,26</sup> *o*-Quinone methides have been suggested as intermediates in the base-catalyzed condensation of phenol with formaldehyde,<sup>27</sup> and their involvement in the HCl-catalyzed RF gel formation is supported by the red color ( $\lambda_{\text{max}} = 543 \text{ nm}$ , Figure 2) developing during the process.<sup>24,28</sup> Thus, *o*-quinone methides may also be attacked by the resorcinol  $\pi$ -system,<sup>27</sup> leading also to  $\text{CH}_2$  bridge formation (eq 6). At this point, it is speculated further that the brick-red color of the RF aerogels may also be associated with a small amount of configurationally locked *o*-quinone methide and/or their spiro derivatives. This hypothesis is consistent with the visual observation that RF aerogels made using a 1:10 R:F molar ratio are much lighter in color than their 1:2 counterparts, signifying less residual *o*-quinone methides. Further support for this hypothesis comes from the fact that submerging RF aerogels in an aqueous  $\text{NaBH}_4$  solution decolorizes them completely, presumably by reduction of *o*-quinone methides to phenols.<sup>28</sup> Indeed, after being washed to remove  $\text{NaBH}_4$  and being exposed to air, gels redevelop their original red color fairly fast. Finally, we need to point out that the acid-catalyzed gelation of our R:F mixtures is exothermic and molds warm up somewhat. But, because of the small size of our samples, no runaway conditions were ever encountered, as has been oftentimes reported during synthesis of novolak resins by the acid-catalyzed reaction of phenol with formaldehyde.<sup>29</sup>

According to the nanomorphology observed in SEM, it seems that polymerization leads to particle formation, followed by phase separation and gelation. SEM results and particle size calculations based on BET surface areas and skeletal densities (Table 1) are internally consistent. Although appearance-wise RF and silica aerogels are very similar (Figure 4), surface areas of RF aerogels are significantly lower than those of silica of similar mesostructure (Table 1), reflecting most probably a less elaborate intraparticle structure, for instance, a simpler primary–secondary particle hierarchy.

Aging seems to be an important factor for shrinkage and therefore for the bulk density of RF aerogels. It is quite remarkable that  $\text{Na}_2\text{CO}_3$ -catalyzed gels not gone through the

$\text{CF}_3\text{COOH}$  treatment swell a lot in acetone and show little structural integrity. On the contrary, similar gels seem more durable after being aged in  $\text{CF}_3\text{COOH}$ , and although they do not swell in acetone, they do nevertheless shrink as much as our HCl-catalyzed gels having gone through aging. Undoubtedly, swelling of the RF networks indicates flexibility. Now, in silica, where the effect of aging has been studied extensively, there are two well-understood processes taking place during aging: syneresis and dissolution/precipitation of silica at points of negative curvature (the interparticle necks).<sup>30</sup> Syneresis (reaction with one another and immobilization of dangling structures on the skeletal backbone) leads to shrinkage, whereas dissolution/precipitation leads to higher mechanical strength. The dissolution/precipitation process is not possible in the case of RF gels because the  $\text{CH}_2$  link formation is not reversible. On the other hand, a syneresis-like mechanism via reaction of dangling  $\text{CH}_2\text{OH}$  groups or *o*-quinone methides with neighboring resorcinol moieties is quite possible. Meanwhile, the ratio of  $\text{CH}_2$  groups in 1:2 and 1:10 RF aerogels (by  $^{13}\text{C}$  NMR) shows that at least with 1:2 RF gels, reaction of R with F is not stoichiometrically complete. Therefore, aging allows for incorporation of more formaldehyde into the network,<sup>31</sup> which in combination with syneresis results in more  $\text{CH}_2$  bridging, and thus in a higher degree of contraction when all pore-filling solvents have been removed. This model is consistent with the trends in shrinkage as a function of the aging time, as well as with the relatively narrow range of surface areas and the particle sizes. No clear trends, however, are identifiable in the skeletal densities, which all fall in the  $1.4\text{--}1.5 \text{ g cm}^{-3}$  range.

## 5. Conclusions

Given the technological relevance of RF aerogels as precursors of carbon aerogels, the long preparation process of the former comprises a bottleneck for the use of the latter. Therefore, accelerating the synthesis of RF aerogels is a very important objective.<sup>32</sup> Resorcinol–formaldehyde gels chemically similar to those obtained by the usual week-long base-catalyzed aqueous gelation process can be made within minutes by acid (HCl) catalysis in  $\text{CH}_3\text{CN}$ . It is reasonable to expect that the major impact of this work will be in the availability and cost of carbon aerogels.

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