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## MATERIALS AND INTERFACES

### Evolution of Ultramicroporous Adsorptive Structure in Poly(furfuryl alcohol)-Derived Carbogenic Molecular Sieves

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The genesis of the adsorptive structure of carbogenic molecular sieves (CMS) derived from poly(furfuryl alcohol) (PFA) was investigated as a function of the synthesis temperature (from 400 to 1200 °C) and soak time (from 0 to 8 h). The apparent CO<sub>2</sub> adsorption capacity of these materials maximizes at 93 mg/g with a final synthesis temperature of 800 °C. The maximum adsorption capacity is obtained from the 24-h CO<sub>2</sub> uptake of 93 mg/g at a relative pressure of 0.015 and at  $T = 295$  K. <sup>13</sup>C CP-MAS NMR spectra of the carbon produced at lower synthesis temperature and short soak times shows a resonance that is reminiscent of the PFA precursor. At higher synthesis temperatures and longer soak times, the NMR spectra display resonances attributable only to aromatic microdomains.

#### Introduction

Adsorptive separation processes have emerged as technologically viable and economically advantageous options to distillation and absorption for some special applications. However, the real potential of adsorptive processes for bulk separations and purifications of gases may not yet be fully realized due to the small number of commercially available selective adsorbents. It is possible that adsorptive separation processes can be more fully exploited if new and more selective adsorbents can be developed within the constraints of economic viability.

Carbogenic molecular sieves (CMS) constitute a new class of adsorbents which are both selective and economically realistic. As a result, these amorphous materials are garnering considerable attention. Their utility for the adsorptive recovery of pure nitrogen from air (Juntgen et al., 1981; LaCava et al., 1989; Nandi and Walker, 1975; Ruthven et al., 1986; Yang, 1987) by pressure swing adsorption has had considerable impact both technologically and commercially. The mechanism for the kinetic separation of nitrogen from air in the CMS is not understood, but clearly it arises from the unique, ultramicroporous structure of these carbons. New processes using CMS for the separation of other gas mixtures, such as *n*-butane from isobutane, or 1-butene from isobutene, may be engineered in the future, if the ultramicropore sizes of the CMS materials can be varied in a controlled fashion over a range of few angstrom units. In addition to controlling the micropore size, engineering the full adsorptive structure of CMS materials also will entail controlling surface functional groups, total surface area, and the ratio of micro- to meso- and macroporosity. Each of these properties is a manifestation of the pathway taken in the conversion of a carbon precursor by pyrolysis to the final CMS structure (Fitzer et al., 1969; Fitzer and Schaefer, 1970; Lafyatis et al., 1991; Lamond et al., 1965).

#### Background

CMS materials are globally amorphous materials devoid of long-range order. Dislocations in the orientation of aromatic microdomains in the glasslike matrix give rise to free volume and ultramicroporosity. The ultramicropores are usually considered to be nearly slit-shaped and the pore mouth dimensions are similar to the diameters of small molecules (Lamond et al., 1965; Wickens, 1990). CMS materials having ultramicropore sizes ranging from 3 to 7 Å have been prepared by pyrolysis of synthetic and natural precursors and by carbon deposition on non-sieving porous carbon (Juntgen et al., 1981; Fitzer et al., 1969; Walker et al., 1965; Gaffney et al., 1990; Cabrera and Armor, 1990). The pore mouth dimensions in CMS are somewhat dependent on the precursors used and the conditions of pyrolytic preparation. Unlike zeolites, CMS show a narrow but real pore size distribution about their mean pore size. For example, a sample of Takeda 5 A carbon will display a standard deviation of about 0.3–0.5 Å, about a mean pore size of 5.5 Å (Chihara et al., 1978). Surface areas, although of dubious value, are reported to range from 300 to 1500 m<sup>2</sup>/g. Pore volumes vary from <0.2 to 0.8 cm<sup>3</sup>/g depending upon the amount of meso- and macroporosity. Due to the absence of long-range order, x-ray diffraction methods are not very effective for characterizing CMS structures. Consequently, the structure must be examined by indirect methods such as the block probe techniques that involve measuring the adsorption of different molecules of different kinetic diameters (CO<sub>2</sub>, 3.3 Å; *n*-butane, 4.3 Å; isobutane, 5 Å; neopentane, 6.2 Å). Micropore diffusivity measurements of probe gases also are useful but are not often reported. On Takeda 5 A CMS Chihara et al. (1978) found that effective diffusivities are activated and are strongly dependent on the kinetic diameter of the probe molecule. This strong dependence of diffusivity on molecular size may be the basis for the commercial recovery of pure nitrogen from air. An oversimplified view is that oxygen has a smaller kinetic diameter (~3.3 Å), thus it diffuses into CMS more rapidly than nitrogen which has a larger kinetic diameter (3.5 Å). As appealing as this mechanistic

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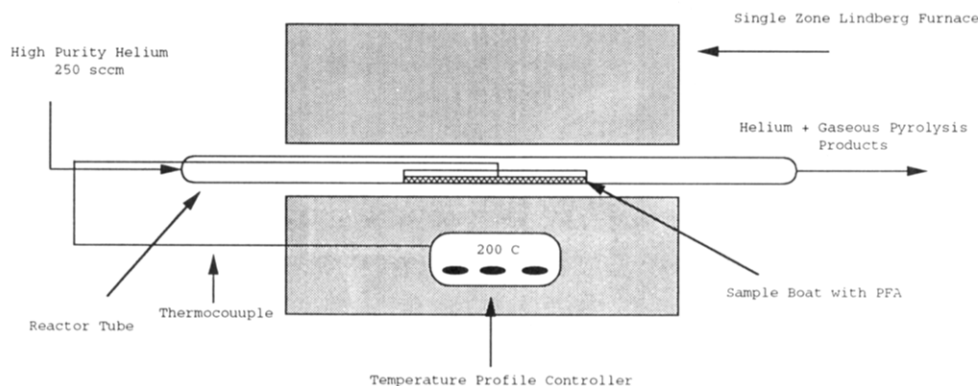


Figure 1. PFA-CMS synthesis reactor schematic.

concept is, it has never been proven and is likely to be deficient when scrutinized thoroughly. However, the kinetic basis for separation is indisputable.

The recovery of nitrogen from air is the first commercial application of this unique adsorbent. However, recent research shows that CMS have been examined for purification of chlorofluorocarbons and hydrochlorofluorocarbons. The ability to remove impurities, namely, hydrogen chloride and hydrogen fluoride from chlorofluorocarbon (Chang, 1990), 2-chloro-1,1-difluoroethylene from 134a (Yates, 1990), and hydrogen fluoride from HFC 134a ( $\text{H}_2\text{C}_2\text{F}_4$ ) (Foley et al., 1991), is ascribed to the molecular sieving effect of the CMS. The extent to which these findings will lead to commercially significant new technologies is as yet unknown. But in these and other examples it is clear that control of the CMS microstructure will play the seminal role in determining how feasible these new processes can become.

Preceding investigators have examined various aspects of polymer pyrolysis mechanisms and the carbogenic materials that result from these processes. In particular, Fitzer and Schaefer and Fitzer et al. (1969, 1970) studied the carbonization of a variety of polymeric resins including furfuryl alcohol resin by analyzing the gases evolved during pyrolysis and studying the infrared spectra of the solids formed at different stages of the thermal treatment. The carbons formed also were analyzed by small angle X-ray scattering, pore volume and BET surface area measurements, as well as water adsorption measurements. They concluded that the chemical structure of the polymeric precursor had little effect on the course of formation of the glasslike carbon, and on its final properties. The glasslike carbon formed had pore mouth openings between 4 and 5 Å, and the lateral pore dimensions were 25–35 Å depending on the heat treatment temperature. On the other hand, from their results, it also was clear that high-temperature heat treatment of the resultant carbon did have an effect on the final pore structure.

The importance of heat treatment temperature on properties of carbons derived from polymeric precursors also was studied by Lamond et al. (1965). In this work the adsorptive properties of carbons derived from Saran and poly(vinylidene chloride) were examined using various probe molecules. The results of this study showed that the slit-shaped pores were responsible for molecular sieving behavior, and the pore constrictions were in the range of 4.5–5.7 Å. Walker et al. (1966) also prepared 4A and 5A molecular sieve from polymeric precursors. Their probe molecule adsorption studies led them to similar conclusions, especially that the pores in these sieves were slit-shaped.

Recently, Lafyatis et al. (1991) investigated the effect of synthesis temperature and time, as well as poly(ethylene

glycol) additives on the adsorptive properties of poly(furfuryl alcohol)-derived CMS. It was shown that higher synthesis temperatures and longer soak times decreased the ultramicropore dimensions. Furthermore, the addition of high molecular weight (>600) poly(ethylene glycol) to the PFA resin produced "transport" pores in the resultant carbon, which provide for more efficient internal mass transport processes.

In this work we have sought to develop a quantitative assessment of the dependence of physical and chemical properties on thermal treatment for one particular carbogenic molecular sieve, that derived from poly(furfuryl alcohol) (PFA-CMS), since it is representative of a class of polymer-derived CMS materials. On the basis of the data accumulated from molecular probe adsorption,  $^{13}\text{C}$ -MAS-SS-NMR, carbon-hydrogen analysis, and X-ray diffraction studies, a physical picture emerges that thermal treatment at high temperatures (600–1000 °C) leads to annealing of the glasslike structure of PFA-CMS. The shrinkage in pore size and free volume that accompanies annealing is manifested at the macroscopic level in the different adsorptive and shape-selective properties of the CMS.

## Experimental Section

**CMS Preparation.** CMS were synthesized by pyrolysis of poly(furfuryl alcohol) (PFA) resin in an inert environment. The PFA resin was obtained from Occidental Chemicals (Durez resin no. 16470). The specific gravity and viscosity of the Durez resin were 1.21 and 2.00 cP at 20 °C, respectively. High-purity helium (99.995%) was obtained from Airco Gas Company. Figure 1 shows the schematic of the pyrolysis reactor setup. The pyrolysis reactor consists of a quartz tube 6 cm in diameter and 110 cm long. The reactor tube was placed inside a Lindberg single zone furnace fitted with a OMEGA CN 2042 temperature profile controller. Approximately 25 g of PFA was charged in a 15-cm-long quartz sample boat. The sample boat was placed in the center of the quartz reactor, and helium was flowed over it at 250  $\text{cm}^3/\text{min}$  (STP). The temperature was accurately maintained and monitored with a thermocouple placed just above the PFA resin surface. The heated zone in the furnace was 30 cm long, and the average axial temperature gradient in the central 25 cm was 0.2 °C/cm. The PFA charge was subjected to the temperature profile shown in Figure 2. The two parameters which were varied were the final synthesis temperature and the time period over which the sample was held at this final temperature, which we will refer to from here on as the "soak time". In Figure 2 the soak time is depicted as the length of time corresponding to the segment AA' at a particular synthesis temperature. The



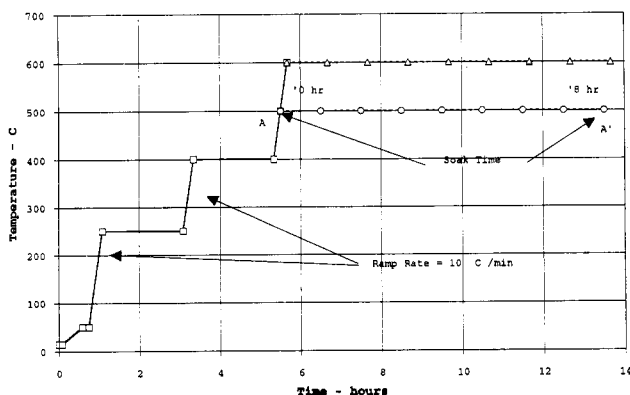


Figure 2. Temperature ramp profile for PFA-CMS synthesis.

Table 1. Experimental Conditions for Probe Gas Gravimetric Uptake Measurements

| probe gas        | press., Torr | rel. press., $P/P^\circ$ | temp., °C |
|------------------|--------------|--------------------------|-----------|
| CO <sub>2</sub>  | 700 ± 3      | 0.015                    | 22 ± 1    |
| <i>n</i> -butane | 492 ± 3      | 0.270                    | 22 ± 1    |
| isobutane        | 605 ± 3      | 0.270                    | 22 ± 1    |

synthesis temperature was varied from 400 to 1200 °C and the soak time from 0 to 8 h. The CMS samples obtained after pyrolysis of PFA resin were washed with acetone and dried in air at 100 °C for 12 h. The CMS yield in all cases was 25 ± 2% of the charge.

**CMS Characterization.** The CMS pore structure was characterized first with gravimetric uptake of CO<sub>2</sub>, *n*-butane, and isobutane. Transient uptakes of *n*-butane and isobutane were measured using a McBain-Bakr balance fitted with a roughing and a turbo pump. Similarly a C. I. microbalance fitted with a roughing and a turbo pump was used to measure CO<sub>2</sub> uptake. Instrument-purity CO<sub>2</sub> was obtained from Keen Gas Company, and instrument-purity *n*-butane and isobutane were obtained from Matheson Gas company. Prior to making the gravimetric uptake measurements of *n*-butane and isobutane, the CMS samples were crushed in three different particle sizes, viz., -60/+80 mesh, -120/+140 mesh, and -170/+200 mesh, and heated to 200 °C under 10<sup>-5</sup>-Torr vacuum for 12–14 h. For CO<sub>2</sub> uptake only -60/+80 mesh particles were used with the same pretreatment. Each of the probe gases was passed through oxygen and moisture traps before exposure to the adsorbent. The experimental conditions for gravimetric uptake measurements are summarized in Table 1.

Elemental analysis of CMS for the carbon and hydrogen content was done at Galbraith Laboratory Inc. (Knoxville, TN). <sup>13</sup>C cross-polarized magic angle spinning solid-state NMR spectra (CP-MAS) were obtained on a 100-MHz M100-S Chemagnetics spectrometer for CMS synthesized at various temperatures and soak times. The conditions of experiments are specified on Figures 10 and 11. Powder X-ray diffraction patterns for CMS synthesized at 500, 800, and 1000 °C and 8 h of soak time were obtained at 295 K on an automated Philips PW1710 machine ( $\theta$ -2 $\theta$  scan mode, Cu K $\alpha$  radiation,  $\lambda$  = 1.5406 Å, graphite monochromator on detector side). The CMS XRD spectra were compared to the synthetic graphite XRD spectrum. SEM micrographs were obtained for CMS synthesized at 600 °C and 8 h of soak time and synthetic graphite on a Phillips 501 microscope.

## Results and Discussion

**Diffusivities and Adsorptive Capacities.** Molecular sieving materials exhibit ultramicropores with critical pore mouth dimensions similar to small molecule kinetic

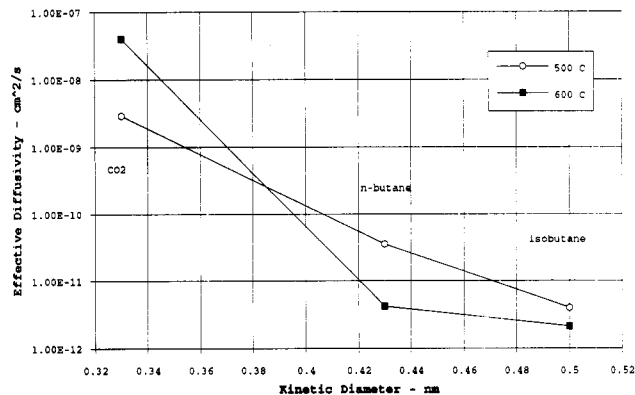


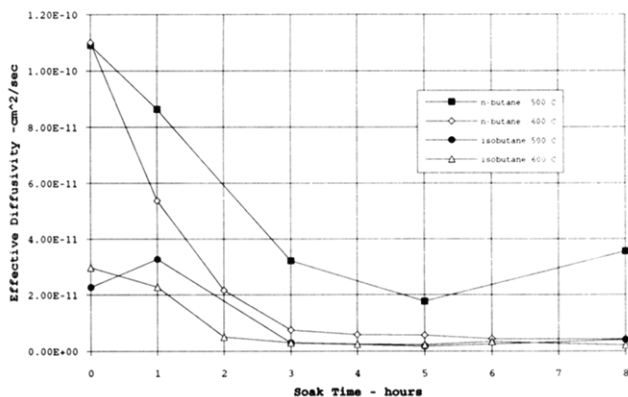
Figure 3. Probe gas effective diffusivity in PFA-CMS synthesized at 500 and 600 °C. Soak time = 8 h.

diameters. This similarity in pore mouth and adsorbate diameters leads to an enhanced interaction between the pore wall and the diffusing molecule. For an adsorbate molecule similar in size to the pore opening, to diffuse through the pore, it must transcend a repulsive energetic barrier. This mode of diffusion is termed "activated". Arguably, CO<sub>2</sub> is a much smaller molecule than *n*-butane or isobutane ( $\sigma_{\text{CO}_2}$  = 3.3 Å,  $\sigma_{n\text{-but}}$  = 4.7 Å, and  $\sigma_{\text{iso}}$  = 5.3 Å); consequently it will experience a lower activation barrier to diffusion through the small, micropore mouth since the repulsive forces will be lower. As a result, CO<sub>2</sub> adsorption will be faster than *n*-butane or isobutane adsorption. Because of these factors, the effective diffusivities of probe gases with different kinetic diameters are indicative of the pore mouth dimensions in CMS samples as well as for other molecular sieves. For isobutane and *n*-butane, the bulk thermodynamic properties are very similar; hence the effective diffusivities measured are a strong function of their size. The ultramicroporosity of carbogenic materials, prepared under different conditions, can be examined by measuring the effective diffusivities of different probe gases, although theory is lacking to link the kinetic diameter of an adsorbate, the pore mouth size, and the effective diffusivity. The effective diffusivities are plotted as a function of the kinetic diameter of the probe gas molecule for PFA-derived CMS samples prepared at 500 and 600 °C for 8 h of soak time (Figure 3). The effective diffusivities were obtained by nonlinear regression analysis of transient adsorption data fitted to the isothermal, single-component sorption equation as described by Ruthven (1984).

$$\frac{M}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left[ -n^2 \pi^2 D_c \frac{t}{r_c^2} \right] \quad (1)$$

Twenty terms in the infinite summation of eq 1 were used to regress the probe gas effective diffusivity. No effort was made in this work to examine the concentration dependence of the effective diffusivities over these samples. Hence the effective diffusivities, although measured under identical conditions, are not absolute but are useful for comparisons of different structural properties between samples.

For the 500 °C sample, the logarithm of the effective diffusivity of the probe gas molecule decreases linearly with the logarithm of the kinetic diameter. Since CO<sub>2</sub> is a smaller molecule, it has an effective diffusivity value several orders of magnitude higher than the *n*-butane and isobutane effective diffusivities. The magnitudes of the effective diffusivities of the two hydrocarbon probes are indicative of a configurational mode of diffusion. For the



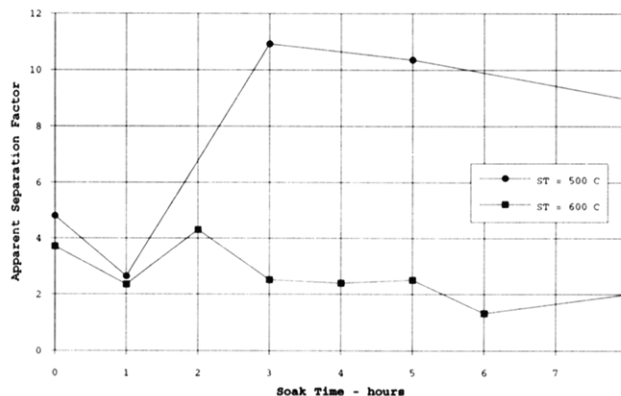
**Figure 4.** Probe gas effective diffusivities as a function of soak time. Parametric in synthesis temperature.

600 °C CMS sample, the effective diffusivity decreases sharply between CO<sub>2</sub> and *n*-butane, but the change in effective diffusivity between *n*-butane and isobutane is less dramatic, since they differ by only a factor of 2 instead of an order of magnitude.

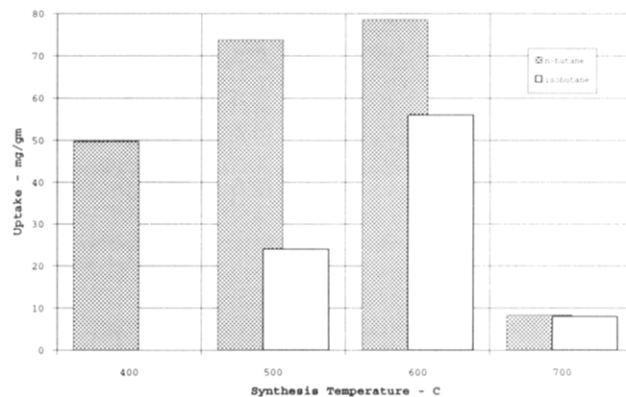
The changes in probe molecule diffusivities within the CMS with soak time and temperature have been examined (Figure 4). The effective diffusivities of *n*-butane and isobutane drop with longer soak times for CMS prepared at 500 and 600 °C. More specifically, the effective diffusivities of *n*-butane in 500 and 600 °C samples decreased from  $1.1 \times 10^{-10}$  to  $3.2 \times 10^{-11}$  and  $4.5 \times 10^{-12}$  cm<sup>2</sup>/s, respectively, for a soak times of 3 h. After approximately 3 h of soak time a nearly constant value for the *n*-butane diffusivity is obtained. Also, it is notable that isobutane effective diffusivities in both the 500 and 600 °C samples are consistently lower than the corresponding *n*-butane effective diffusivities, until approximately 3 h of soak time, after which they approach the *n*-butane effective diffusivity for the CMS samples synthesized at 600 °C. Isobutane is expected to have a lower effective diffusivity than *n*-butane since isobutane has a larger kinetic diameter.

The *n*-butane effective diffusivities are consistently lower for the CMS samples synthesized at 600 °C with the exception of the one prepared at 600 °C but without any soaking step at 600 °C. The isobutane effective diffusivities are similar in magnitude for CMS samples prepared at either 500 or 600 °C with shorter soak times (<1 h). The initial soak time effect shows the narrowing of the critical pore mouth dimensions. To convey the effect of synthesis temperature on the magnitude of *n*-butane and isobutane diffusivities, the ratio of the *n*-butane to isobutane diffusivities, or the apparent separation factor, is plotted as a function of the soak time for CMS samples synthesized at 500 and 600 °C (Figure 5). Clearly, the ratio at zero soak time is similar for the 500 and 600 °C CMS. However, beyond approximately 1 h of soak time, the effective diffusivity ratios for the 500 °C CMS increase to approximately 10, while those for the 600 °C CMS samples gradually decrease to approximately 1.7. It is interesting to note that the large ratios for the *n*-butane to isobutane diffusivities indicate that the CMS samples synthesized at 500 °C potentially may be exploited for the separation of these gas mixtures.

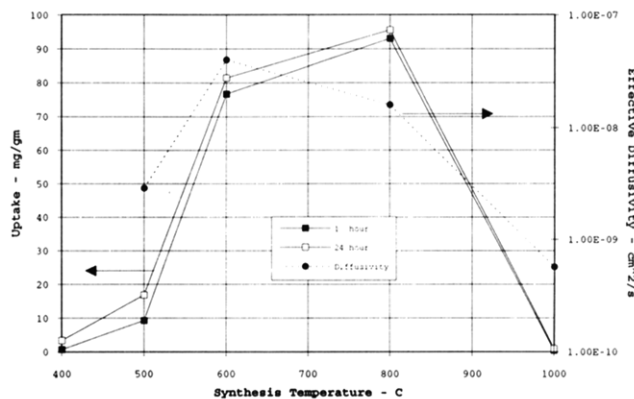
In order to determine whether the drop in effective diffusivities was due to a change in pore size or a change in capacity, in other words the  $M_{\infty}$  value in eq 1, the 24-h uptakes for *n*-butane and isobutane were obtained for samples prepared at 400, 500, 600, and 700 °C and with 3 h of soak time (Figure 6). The 24-h uptake represent a pseudoequilibrium uptake and are indicative of the



**Figure 5.** Apparent separation factor as a function of soak time for PFA-CMS synthesized at 500 and 600 °C.



**Figure 6.** Twenty-four hour probe gas uptake as a function of synthesis temperature. Soak time = 3 h.



**Figure 7.** CO<sub>2</sub> effective diffusivity and uptake on PFA-CMS as a function of synthesis temperature. Soak time = 8 h.

available capacity and hence free volume within the CMS pores. The pseudoequilibrium uptakes of *n*-butane and isobutane maximize for the samples prepared at a temperature of 600 °C. However, the effective diffusivities of *n*-butane and isobutane are higher for the CMS samples prepared at 500 °C. Thus the narrowing of the pore mouth dimensions has led to a decrease in the effective diffusivity of *n*-butane and isobutane. To elucidate this matter further, the effective diffusivities, as well as the 1- and 24-h uptakes of CO<sub>2</sub> were obtained for CMS samples synthesized at various temperatures (400–1000 °C) and 8 h of soak time (Figure 7). For CMS synthesized at 500 °C, the effective diffusivity of CO<sub>2</sub> is  $2.9 \times 10^{-9}$  cm<sup>2</sup>/s and increases to  $4 \times 10^{-8}$  cm<sup>2</sup>/s for CMS synthesized at 600 °C. Beyond 600 °C, the magnitude of the CO<sub>2</sub> effective diffusivity decreases with increase in synthesis temperature. On the other hand, the 24- and 1-h uptakes maximize for CMS synthesized at 800 °C. The 24-h uptake

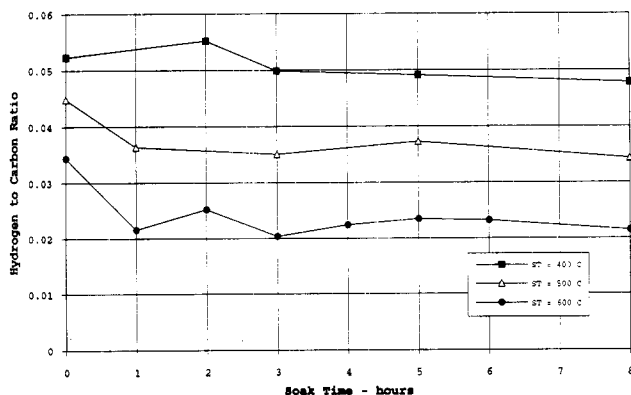


Figure 8. Hydrogen to carbon ratio as a function of soak time for PFA-CMS synthesized at 400, 500, and 600 °C.

is representative of the free volume available for adsorption, and it indicates that this free volume or capacity is lower for the CMS synthesized at lower temperature. For the PFA-derived CMS in this study the temperature at which the capacity maximizes is close to that which we reported earlier (Lafyatis et al., 1991). However, for Saranderived CMS, the temperature of maximum capacity shifts to 1000 °C (Lamond et al., 1965). This shift in temperature for capacity maximization presumably is a result of the different chemical structures of the two precursors and the different pyrolysis chemistries that they undergo which lead to different CMS microstructures. These soak time and temperature effects on the uptakes and diffusivities of CO<sub>2</sub>, *n*-butane, and isobutane on PFA-CMS suggest that the microstructure of these materials is still evolving at low temperatures and short soak times (<3 h).

**Chemical Analysis and <sup>13</sup>C-CP-MAS-SS.** To probe the chemical changes that accompany microstructure evolution, elemental analyses were done on some of the CMS samples. The hydrogen to carbon ratios for PFA-CMS samples synthesized at 400, 500, and 600 °C and different soak times were determined (Figure 8). In all the cases, the hydrogen to carbon ratio decreases at early soak times and then approaches a lower limiting value at longer soak times. The hydrogen to carbon ratio for all the soak times examined is consistently lower for CMS samples synthesized at progressively higher temperatures. Hence the decrease in the hydrogen to carbon ratio is favored by higher temperature and longer soak times, conditions that also lead to decreases in the magnitudes of probe gas effective diffusivities. At short time the CMS structure is developed through condensation and aromatization reactions, accompanied by loss of hydrogen. Such reaction schemes have been proposed for CMS derived from phenol-formaldehyde resins and furfuryl alcohol-formaldehyde resins (Fitzer et al., 1969). The constant but different values of the hydrogen to carbon ratio at long soak times for any given temperature indicates that the CMS samples evolve toward a metastable equilibrium structure. Different metastable equilibrium states are attained for the CMS samples synthesized at different temperatures and long soak times. To gain more insight into the temperature dependence of the hydrogen to carbon ratio, a series of CMS samples were prepared at 400, 500, 600, 800, 1000, and 1200 °C and 8 h of soak time. The hydrogen to carbon ratio is seen to drop exponentially with increasing temperature to a state of the material that is essentially hydrogen-free above 1000 °C (Figure 9). Thermodynamically, this makes sense, since the state to which the system is evolving is polycrystalline graphite.

To probe the chemistry of microstructure evolution further, <sup>13</sup>C-CP-MAS-SS NMR studies were done on the

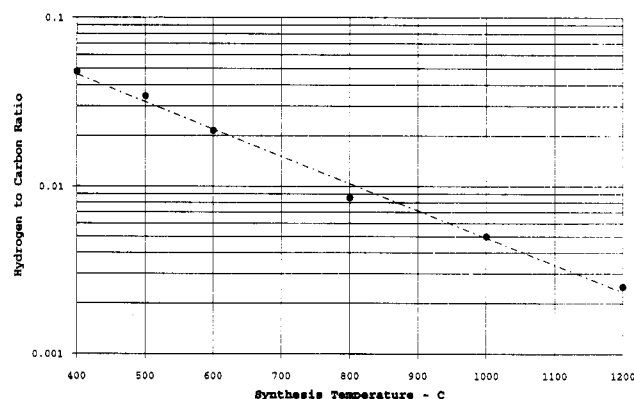


Figure 9. Hydrogen to carbon ratio as a function of synthesis temperature. Soak time = 8 h.

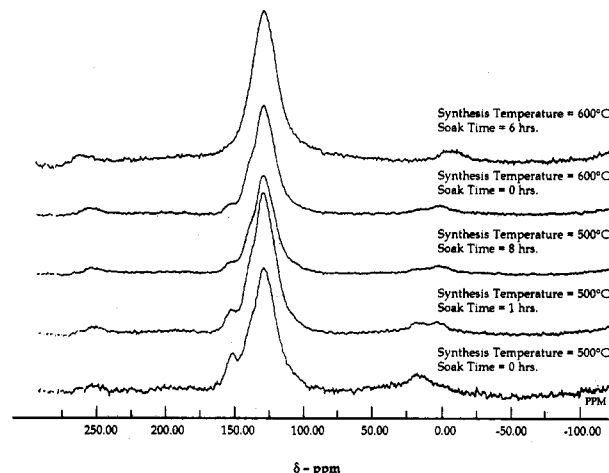
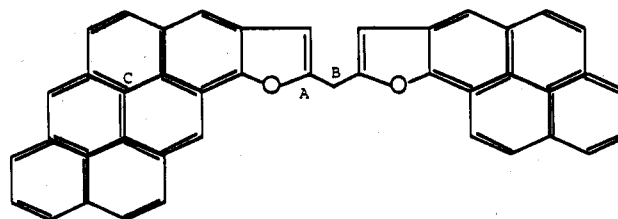
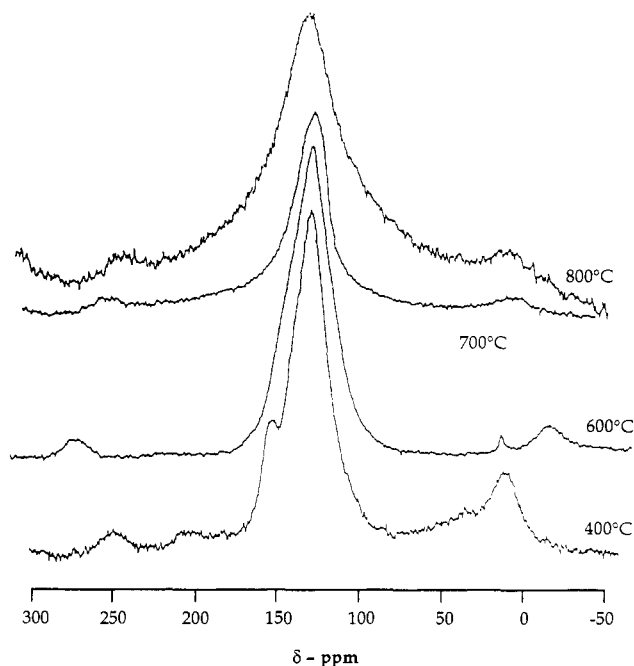


Figure 10. <sup>13</sup>C CP-MAS solid-state NMR of PFA-CMS. In all cases pulse width = 6.5 μs, pulse delay = 1 s, contact time = 1 ms, NA = 10 000.

CMS samples. Figures 10 and 11 show the solid-state NMR spectra for CMS samples synthesized under different conditions. For the samples prepared at 400 °C–8-h soak time and 500 °C–0-h soak time, three prominent resonances are observed at approximately 20, 126, and 150–152 ppm. [Symmetric spinning side bands also are seen at ~25 and 250 ppm.] The 126 ppm resonance is the most prominent and is attributed to an sp<sup>2</sup> hybridized carbon (marked C) in the structural model of the aromatic microdomain. The broad peak at ~20 ppm (Figure 11) is



due to the presence of sp<sup>3</sup> hybridized carbon (marked B), and the 150–152 ppm peak is attributed to a sp<sup>2</sup> carbon in the proximity of an oxygen linkage (marked A). These resonances compared well to the positions of resonance attributed to similar carbon sites in furfuryl alcohol resins of different viscosities (Chuang et al., 1979). The resonances at ~20 and ~152 ppm decrease relative to the 126 ppm resonance and eventually disappear at higher synthesis temperatures and longer soak times. This implies that the sp<sup>3</sup> carbons react earlier than the sp<sup>2</sup> carbons next to the oxygen atom. The resonance due to sp<sup>2</sup> carbon



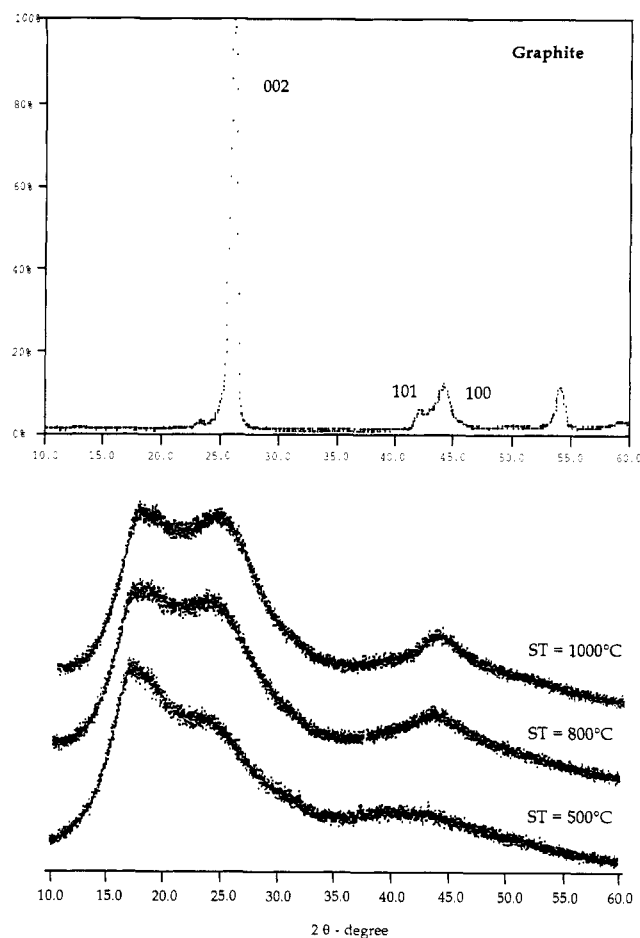
**Figure 11.**  $^{13}\text{C}$  CP-MAS solid-state NMR of PFA-CMS prepared at different synthesis temperature and 8 h of soak time. For 400, 600, and 700 °C samples pulse width = 6.5  $\mu\text{s}$ , pulse delay = 3 s, contact time = 1 ms. For 800 °C sample pulse width = 8.8  $\mu\text{s}$ , pulse delay = 2 s, contact time = 2 ms. For 400 and 700 °C, NA = 25 000. For 600 °C, NA = 18 000. For 800 °C, NA = 50 000.

next to the oxygen atom is barely seen in CMS samples prepared at 600 °C for 0 h of soak time. However, the 126 ppm resonance is the most prominent and is present in all the samples.

The presence of resonances attributed to the  $\text{sp}^3$  and  $\text{sp}^2$  carbons near an oxygen atom in CMS prepared at low synthesis temperatures and short soak times indicates that some structural vestiges of the original precursor are still preserved. At lower synthesis temperatures, aromatization as well as condensation reactions take place, using up the residual oxygen and hydrogen atoms, and lead to the development of the pore structure in CMS. At higher synthesis temperatures and longer soak times, the resonance assigned to the  $\text{sp}^3$  carbons collapses and only the resonance due to  $\text{sp}^2$  carbons is observed. These  $\text{sp}^2$  carbons form the basis for the aromatic microdomains.

The residual oxygen atoms slow the growth of the aromatic domain and make the low-temperature carbon structure more accessible to probe molecules. The oxygen atom linkages induce disorder in the structure of the carbon and thereby aid in maintaining the large micropore pore mouth dimensions of the carbon. At higher temperatures, due to a large influx of thermal energy, the oxygen linkages along with the residual carbon-hydrogen bonds are readily broken (Jenkins and Kawamura, 1976). This leads to the fusion of the aromatic domains and thus a collapse of the micropores. Hence the oxygen atoms help maintain microporosity in PFA-derived carbons. It should be noted that, for CMS samples prepared above 600 °C, the elemental analysis indicates only the presence of carbon and less than 0.5% hydrogen. Thus the narrowing of pores at higher synthesis temperatures may be due largely to the growth of the aromatic microdomains, and a concomitant adjustment in their orientation, leading to higher ordering at the expense of the residual oxygen atoms.

**X-ray Diffraction and SEM.** Figure 12 compares the powder X-ray diffraction patterns for the CMS samples prepared at 500, 800, and 1000 °C for 8 h of soak times with that for synthetic graphite (obtained from Aldrich



**Figure 12.** Powder X-ray diffraction patterns for synthetic graphite and PFA-CMS. PFA-CMS soak time = 8 h.

Chemicals). The 002, 100, and 101 peaks at scattering angles of 26°, 43°, and 41°, respectively, for synthetic graphite are marked in the figure. The 002 peak is derived from spacing between graphite sheets, the 100 peak is related to the distance between carbon atoms within a graphite sheet, and the 101 peak is related to the extent to which the extensive graphite sheets are in ABA register. A definite 101 peak is necessary to define a carbon as graphite (Jenkins and Kawamura, 1976).

The powder X-ray diffraction profile of CMS synthesized at 500 °C shows a very broad and asymmetric line at about 17° with a shoulder at 23°. This diffraction band can be divided into two symmetric bands at 17° and 23° corresponding to average  $d_{002}$  spacing of 0.52 and 0.39 nm. A very broad band with no definite maximum is also observed between 35° and 50° scattering angles. This band corresponds to  $d_{100}$  spacing between carbons. The large average  $d_{002}$  spacing indicates that the aromatic sheets in this CMS are further apart than are the layers in graphite ( $d_{002} = 0.335$  nm). The low-intensity broad band between 35° and 50° also indicates that aromatic sheets are barely formed at this stage of CMS synthesis. The broad band also indicates that the average microcrystallite size is very small since the width of the peak is inversely proportional to the crystallite size. The high intensity peak at 17° is not clearly understood. Jenkins and Kawamura (1976) suggest that this peak may arise due to polymer molecules being converted into narrow ribbons of aromatic molecules linked by C-C bonds or due to stacking of the aromatic ribbons.

In the powder X-ray diffraction patterns for CMS synthesized at 800 and 1000 °C, the position of the 002



line shifts to  $24^\circ$  and  $25^\circ$ , respectively, and distinct peaks are observed. The shift in the scattering angle corresponds to a decrease in average  $d_{002}$  spacing from 0.39 nm to 0.37 nm at  $800^\circ\text{C}$  and 0.356 nm at  $1000^\circ\text{C}$ . However, the average  $d_{002}$  spacing in CMS is very large. For randomly oriented graphite layers, the average interlayer spacing is 0.344 nm (Jenkins and Kawamura, 1976). The 100 line also shows a definite maximum at  $44^\circ$  and position of the peak does not change, but the 100 line becomes narrower. The narrowing of the 100 peak indicates a modest increase in the aromatic crystallite size. The peak attributed to the ribbonlike formation or stacking of ribbons at  $17^\circ$  remains invariant with respect to the width, the intensity, and the position for all the CMS. This implies that the average distance between the stacked aromatic ribbons is constant, or that the size of the ribbons is not changing.

The powder X-ray diffraction patterns of CMS allow us to draw some conclusions about their low-temperature structures. The structure of  $500^\circ\text{C}$  CMS is chaotic and at best only very short-range order is observed, since the aromatic domains are barely formed. The random orientation of small aromatic domains may give rise to the stacked-ribbon-like structure as shown by the line at  $2\theta = 17^\circ$ . For CMS synthesized at higher temperatures, the aromatic microdomains grow and the interlayer spacing between aromatic sheets decreases. The long-range structure is still highly chaotic, but increased short-range order begins to appear in these structures. The presence of a ribbonlike structure, or the stacked-ribbon-like structure, is existent at higher synthesis temperatures. Hence the structure of CMS synthesized at higher temperatures is not close to that of graphite. The presence of aromatic carbon was also confirmed by the  $^{13}\text{C}$  CP-MAS-SS NMR.

Figure 13 shows the SEM photographs of CMS prepared at  $600^\circ\text{C}$  and 8 h of soak time. No preferred order is seen for cleavage or cracking of the CMS particles. The particles also lack any visible texture or structure. No large pores are observed, and the particle's appearance is best described as glassy. Glassy carbons are characterized by structural isotropy and lack of texture or structure (Jenkins and Kawamura, 1976). In contrast, the graphite particles are flaky and uniform in appearance and have considerable structural anisotropy.

### Implications for Microstructure of PFA-Derived CMS

In this paper, we have referred to the carbonaceous molecular sieves as carbogenic molecular sieve, and this terminology deserves some elaboration. The sieves synthesized from PFA or other polymer precursors are not absolutely pure carbons, but contain hydrogen, oxygen, halogens, and traces of other elements chemically bonded to the carbon. These non-carbon elements may play a very important role in developing the molecular sieving structures of these materials, as well as influencing their interactions with adsorbed molecules. Hence these materials are best referred to as carbogenic molecular sieves, meaning that they contain other elements along with carbon (Corey and Cheng, 1988).

The effective diffusivity measurements, elemental analysis, solid-state NMR spectroscopy, and X-ray diffraction results allow us to draw some conclusions about the evolution of the ultramicroporous structure. From the diffusivity and 24-h uptake measurements, it is evident that the pore mouth dimensions narrow as the synthesis temperature increases. The soak time also narrows the pore mouth dimension in CMS as the structure evolves toward a metastable equilibrium state at any particular



**Figure 13.** SEM micrographs of PFA-CMS and synthetic graphite (reproduced at 65% of original size). (top) PFA-CMS:  $600^\circ\text{C}$ , 8 h,  $320\times$ , 30 keV, scale =  $10\ \mu\text{m}$ . (bottom) Graphite:  $640\times$ , 90 keV, scale =  $10\ \mu\text{m}$ .

synthesis temperature. Some vestiges of the CMS precursor are preserved in the solid prepared at lower pyrolysis and soak temperatures. These residual elements of the furanic structure react at higher temperatures and longer soak times with a simultaneous narrowing of the pore mouth dimensions and development of the adsorptive capacity. The drop in the measurable amount of hydrogen and oxygen in the CMS also seems correlate with longer time, high-temperature structural transformations taking place. The two observations may be coupled if both arise from consumption of residual furanic species in the carbogenic structure. The presence of aromatic microdomains is confirmed by both the XRD and  $^{13}\text{C}$ -CP-MAS-SS NMR results; however these aromatic microdomains are extremely small and are chaotically oriented in the structure of the CMS.

The adsorption measurements in conjunction with the NMR and XRD results allow us to propose a physical picture for the formation of ultramicropores and the changes associated with them as a function of the synthesis temperature and time (Figure 14). Upon pyrolysis of PFA, at low temperatures ( $200$ – $500^\circ\text{C}$ ), a highly chaotic structure consisting of amorphous carbon and very small aromatic microdomains are formed. This structure has a critical average pore dimension of  $r_{\text{pore},1}$  which is fairly large. This low-temperature structure may have some reminiscence of the original precursor, thereby increasing the overall disorder of the material and its porosity.

At higher temperatures and longer soak times, the size of the aromatic microdomains increases at the expense of



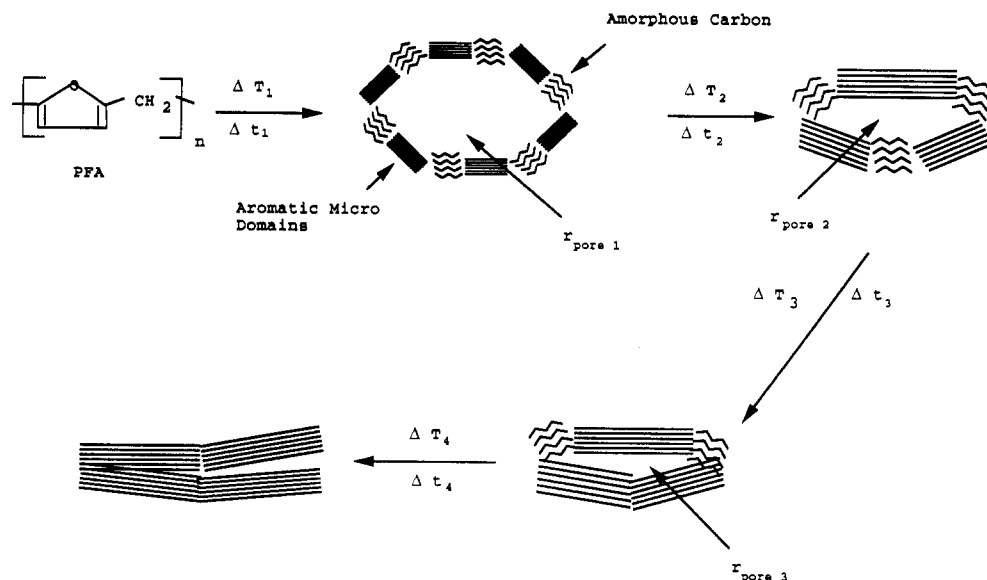


Figure 14. Conceptual model for adsorptive structure evolution in PFA-derived CMS.

the amorphous carbon regions, and hence a slightly more ordered structure is formed in the short range, but it is still highly disordered over the long range. As aromatic microdomains slowly grow with longer time at fixed temperature or higher temperature, the order in the structure increases. At the same time the misalignment between the aromatic microdomains begins to diminish, and with it the average pore mouth dimension decreases in size. In other words, it is the misalignment of the aromatic microdomains that gives rise to the ultramicroporosity in the carbon. At high degrees of misalignment, the pores are larger and numerous. As the degree of misalignment decreases, the pores narrow, and eventually the overall porosity drops. Hence  $r_{\text{pore},2}$  (Figure 14) is, on average, nominally less than  $r_{\text{pore},1}$ . As the material is heated to a higher temperature, the internal growth of the aromatic microdomains continues, and the amorphous carbon is consumed. Eventually, with longer time or higher temperature, the micropore structure will collapse, as the microdomains enlarge and more completely align with one another.

In essence, the time and temperature effects can be thought of as an annealing process which in the limit leads to a nearly nonadsorptive, microcrystalline graphite structure (Franklin, 1950, 1951). Hence, the two extreme ends of this structural spectrum are furfuryl alcohol monomer, which has a negative heat of formation ( $\Delta H_f^\circ = -49$  kcal/mol), and graphite ( $\Delta H_f^\circ = 0$  kcal/mol), which defines the standard state of solid carbon. The driving force for conversion of furfuryl alcohol into graphite or a graphite-like solid is supplied by elimination of small molecules including  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{CH}_4$  among others. This is the same driving force that leads to the carbogenic molecular sieves. Since this transformation is essentially irreversible, the CMS structures can be considered as intermediates that are nonequilibrium or metastable states. As a result, their physical properties should be highly path dependent, as our results indicate they are.

With this in mind we can address the difference between the graphitizing (PVC) and non-graphitizing (PFA, PVDC, etc.) polymer-derived carbons. The extent to which a pathway is available within the solid will determine whether or not it will transform to graphite at elevated temperature in a reasonable, laboratory time frame. The low-temperature solid structures that result from so-called non-graphitizing polymers like PFA are in essence "ki-

netically frozen" by cross-links that form between chains in the precarbonized solid. If the cross-linking density is high, then the pathway to the graphitic structure is much higher in energy and much less favorable, thus requiring much higher temperatures and longer times to achieve than in a less cross-linked or non-cross-linked precursor. The covalent bonds that form the cross-links prevent the facile rearrangement of the constituent atoms in the structure, rearrangements that must take place in order for graphitization to proceed. These ideas are borne out not only by our results, but by those of previous researchers, especially when PFA-derived carbon is compared to PVC-derived carbon (Rand and McEnaney, 1985; Jenkins and Kawamura, 1976; Maire and Méring, 1970; Fischbach, 1971; Pacault, 1971). Hence a cohesive physical picture emerges for the structures of these carbogenic solids that can be used to describe either graphitizing or non-graphitizing polymer-derived carbons.

## Conclusions

From the probe gas adsorption studies, elemental analyses, solid-state NMR spectroscopy, and X-ray diffraction results, it is evident that soak time and synthesis temperature are key parameters for controlling the adsorptive structure of PFA-derived CMS. Higher synthesis temperatures and longer soak times lead to a CMS with apparently narrower pores, when compared to a CMS prepared at lower temperatures or soak times. The narrowing of the pores moderately affects the already low effective diffusivities of *n*-butane and isobutane, but markedly changes the  $\text{CO}_2$  diffusivities by several orders of magnitude. The  $^{13}\text{C}$  CP-MAS-SS NMR spectra indicate that the presence of the furanic carbon rings may play a seminal role in the low-temperature structure of the CMS and, hence, for the efficacy of transport of gas molecules.

The effect of time and temperature on the CMS properties is best understood as an annealing of the glassy microstructure that leads to larger aromatic microdomains with better alignment and order, less free volume for gas adsorption and diffusion, and, ultimately, lower total free energy.

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### Literature Cited

- Cabrera, A. L.; Armor, J. N. United States Patent 5,071,450, 1991.
- Chang, C. Applied for United States Patent, 1990.
- Chihara, K.; Suzuki, M.; Kawazoe, K. Interpretation of Micropore Diffusivities of Gases in Molecular Sieving Carbon. *J. Colloid Interface Sci.* 1978, 65, 584-587.
- Chuang, I.; Maciel, G. E.; Myers, G. E.  $^{13}\text{C}$  NMR Study of Curing in Furfuryl Alcohol Resin. *Macromolecules* 1984, 17, 1087-1090.
- Corey, E. J.; Cheng, X. M. *The Logic of Chemical Synthesis*; John Wiley & Sons: New York, 1988; pp 1-2.
- Fischbach, D. B. The Kinetics and Mechanism of Graphitization. In *Chemistry and Physics of Carbon*; Walker, P. L., Jr., Ed.; Marcel Dekker: New York, 1971; Vol. 7, pp 1-106.
- Fitzer, E.; Schaefer, W. The Effect of Crosslinking on the Formation of Glasslike Carbon from Thermosetting Resin. *Carbon* 1970, 8, 353-364.
- Fitzer, E.; Schaefer, W.; Yamada, S. The Formation of Glass Like Carbon by Pyrolysis of Polyfurfuryl Alcohol and Phenolic Resin. *Carbon* 1969, 7, 643-648.
- Foley, H. C.; Mariwala, R. K.; Manzer, L. Applied for United States Patent, 1993.
- Franklin, R. E. The Structure of Graphitic Carbon. *Acta Crystallogr.* 1950, 4, 253-261.
- Franklin, R. E. Crystallite Growth in Graphitizing and Non-Graphitizing Carbons. *Proc. R. Soc. (London)* 1951, A209, 196.
- Gaffney, T. R.; Farris, T. S.; Cabrera, A. L.; Armor, J. N. United States Patent 5,098,880, 1992.
- Jenkins, G. M.; Kawamura, K. *Polymeric Carbons-Carbon Fiber, Glass and Char*; Cambridge University Press: London, 1976; pp 12-13.
- Juntgen, H.; Knoblauch, K.; Harder, K. Carbon Molecular Sieves: Production from Coal and Application in Gas Separation. *Fuel* 1981, 60, 817-822.
- LaCava, A. I.; Koss, V. A.; Wickens, D. Non-Fickian Adsorption Rate Behaviour of Some Carbon Molecular Sieves. I. Slit-Potential Rate Model. *Gas. Sep. Purif.* 1989, 3, 180-186.
- Lafyatis, D. S.; Tung, J.; Foley, H. C. Poly(furfuryl alcohol)-Derived Carbon Molecular Sieves: Dependence of Adsorptive Properties on Carbonization Temperature, Time and, Poly(ethylene glycol) Additives. *Ind. Eng. Chem. Res.* 1991, 30, 865-873.
- Lamond, T. G.; Metcalfe, J. E., III; Walker, P. L., Jr. 6Å Molecular Sieve Properties of Saran Type Carbons. *Carbon* 1965, 3, 59-63.
- Maire, J.; Méring, J. Graphitization of Soft Carbons. In *Chemistry and Physics of Carbon*; Walker, P. L., Jr., Ed.; Marcel Dekker: New York, 1970; Vol. 6, pp 125-190.
- Nandi, S. P.; Walker, P. L., Jr. Carbon Molecular Sieves for the Concentration of Oxygen from Air. *Fuel* 1975, 54, 169-178.
- Pacault, A. The Kinetics Graphitization. In *Chemistry and Physics of Carbon*; Walker, P. L., Jr., Ed.; Marcel Dekker: New York, 1971; Vol. 7, pp 107-154.
- Rand, B.; McEnaney, B. Carbon Binders from Polymeric Resins and Pitch. Part I-Pyrolysis Behaviour and Structure of the Carbon. *Br. Ceram. Trans. J.* 1985, 84, 157-165.
- Rudnick, L. R. United States Patent 4,577,049, 1986.
- Ruthven, D. M. *Principles of Adsorption and Adsorption Processes*; John Wiley & Sons: New York, 1984; pp 167-173.
- Ruthven, D. M.; Raghavan, N. S.; Hassan, M. M. Adsorption and Diffusion of Nitrogen and Oxygen in a Carbon Molecular Sieve. *Chem. Eng. Sci.* 1986, 41, 1325-1332.
- Walker, P. L.; Lamond, T. G.; Metcalfe, J. E., III. The Preparation of 4A and 5A Carbon Molecular Sieves. In *Proceedings of the Second Conference on Industrial Carbon and Graphite*; Society of Chemical Industry: London, 1966; pp 7-14.
- Wickens, D. A. A. Generalization of the Slit-Model of Pores in Microporous Carbon. *Carbon* 1990, 28, 97-101.
- Yang, R. T. *Gas Separation by Adsorption Processes*; Butterworths: Boston, 1987.
- Yates, S. F. United States Patent 4,906,796, 1990.

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