Genesis of porosity in polyfurfuryl alcohol derived nanoporous carbon

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Abstract

The pyrolysis of polyfurfuryl alcohol was studied up to 600 °C. Micropores appear in the carbon as early as 300 °C along with a significant amount of mesopores. As the pyrolysis temperature is increased, microporosity is retained, but the mesoporosity disappears. At 600 °C the material is microporous with a monodisperse pore size distribution centered at 4–5 Å. Infrared, X-ray photoelectron, and nuclear magnetic resonance spectroscopies, in combination with thermogravimetric analysis provide evidence that between 300 and 400 °C, both polyaromatic domains decorated with hydrogen and oxygen (hetero) atoms and partially decomposed polymer chains coexist. The unreacted polymer and heteroatoms induce mesoporosity by buffering the micropores created by polyaromatic domains. Raising the pyrolysis above 400 °C releases the buffering material, thereby collapsing the mesopores.

Keywords: Pyrolysis; Porous carbon; Nuclear magnetic resonance; Infrared spectroscopy; Molecular sieves

1. Introduction

Pyrolysis of the thermosetting polymer polyfurfuryl alcohol (PFA) leaves nanoporous carbon (NPC), which is inherently microporous with a very narrow pore size distribution centered at 4–5 Å [1,2]. The micropores act as molecular sieves, which makes NPC appealing for a number of applications, including catalysis and gas separation [3,4]. Understanding the origins of pore formation is critical to engineering the carbon to meet specific requirements of these applications.

Fitzer and Schafer utilized infrared spectroscopy (IR) to examine the pyrolysis of PFA in detail [5,6]. The furan ring was found to be stable up to 275 °C. Between 300 and 400 °C the furan ring ruptured and released CO, CO₂, and H₂O. Aromatic units appeared around 400 °C as the fragments began to coalesce. At temperatures greater than 450 °C a reaction of the remaining methylene bridges with water to form keto groups was proposed. In the same temperature range, formation of methane ceased due to the oxidation of methylene bridges and a significant amount of hydrogen was released. The authors speculated that in the intermediate state between the polymer and the final carbon, open pores with diameters smaller than 100 Å must be present that allowed the transport of gaseous products formed during the pyrolysis. There was no experimental evidence given to prove this hypothesis.

In order to understand further the pyrolysis process the NPC formed by decomposition of PFA has been characterized over a range of temperatures by several other techniques, which include gas adsorption, Raman spectroscopy, X-ray diffraction, and nuclear magnetic resonance spectroscopy (NMR)[1,2,7–10]. The origin of microporosity in these carbons has been addressed via a pair distribution function method [11–13]. It was shown that in addition to...
six-membered rings the aromatic domains include five- and seven-membered rings, which induces curvature of the domains, unlike graphite. Curvature causes misalignment of the aromatic domains, and thereby creates micropores between the disordered sheets. Mariswala et al. noted cross-linking in PFA leads to micropore formation and to the resistance to graphitization that is well known in NPC [2]. This relationship between polymer cross-linking and non-graphitizing microporous carbon has also been demonstrated in the polyvinylchloride (PVC) – polydivinylchloride (PVDC) system [14].

The mechanism of furfuryl alcohol polymerization is cationic and cross-linking occurs readily. Choura et al. extensively studied the cross-linking reaction in polyfurfuryl alcohol, with the aid of model compounds [15]. The authors suggested cross-linking requires that mobile hydrogen atoms, present on the polymer backbone in the form of CH$_2$ groups, undergo a series of hydride ion abstraction and proton expulsion reactions, which leaves the polymer highly conjugated. It is the conjugated structure that reacts to form a cross-link, either by condensing with the propagating center on another chain or with a furan ring (diene) in a Diels–Alder reaction.

The present investigation follows the development of micropores and provides the first experimental evidence of the autogenesis of mesoporosity in PFA derived NPC at temperatures between 25 and 500 °C. The development of the carbon structure has been studied by gas adsorption, IR, X-ray photoelectron spectroscopy (XPS), NMR, and thermogravimetric analysis (TGA).

2. Experimental

2.1. Synthesis and pyrolysis of polyfurfuryl alcohol (PFA)

0.1 M $p$-toluenesulfonic acid monohydrate (Sigma–Aldrich) was dissolved in 5 ml of tetrahydrofuran (THF, spectroscopic grade Sigma–Aldrich) and the reaction mixture was cooled in an ice bath. To this solution, 10 ml of furfuryl alcohol (FA, 99% Sigma–Aldrich) was slowly added by a syringe pump at a rate of 10 ml h$^{-1}$. The polymerization reaction was allowed to proceed for 48 h at 25 °C. The resultant polymer was pyrolyzed under flowing argon in a quartz tube furnace, which was heated at $10^\circ$C min$^{-1}$ to a final temperature between 100 and 600 °C and allowed to soak for 1 h.

2.2. Characterization of PFA and PFA-derived nanoporous carbon

The pyrolysis of PFA was monitored by a TA Instruments TGA 2050. The sample was heated under a flowing argon atmosphere at $10^\circ$C min$^{-1}$ to 800 °C. Gaseous by-products were passed through a ThermoStar mass spectrometer (Pfeiffer, Nashua, NH).

The chemical structure of the pyrolyzed residue was studied using a Nexus 670 FTIR spectrometer in transmission mode. The carbon samples were mixed with FTIR grade potassium bromide (Sigma–Aldrich) in a 1:99 weight ratio and pressed into a pellet under 5000 psig pressure. XPS analyses were performed on a monochromatic AlK$\alpha$ source with a Kratos Axis Ultra (England) instrument. Spectra were collected with a photoelectron takeoff angle of 90° and 20 eV pass energy.

Solid-state $^{13}$C NMR was also utilized as a structural probe. Spectra were collected using a $^1$H to $^{13}$C variable amplitude CP-MAS technique implementing TOSS (total suppression of spinning sidebands) and TPPM (two pulse phase modulation) $^1$H decoupling. PFA25 and PFA100 were analyzed on a 125-MHz Chemagnetics Varian CMX-Infinity 500 spectrometer with $^1$H $\pi/2$ pulse width = 5.3 μs, contact time = 6 ms, and spin rate = 6 kHz. The spectra of PFA200, PFA300, and PFA400 were measured on a 75-MHz Chemagnetics Varian CMX-Infinity 300 with $^1$H $\pi/2$ pulse width = 3.95 μs, contact time = 1 ms, and spin rate = 3 kHz.

A methyl chloride adsorption isotherm was used to calculate the total pore volume and the average pore size of the carbons according to the Horvath–Kawazoe and the Kelvin models in the micro- and mesopore regions, respectively. A slit pore shape was assumed for pores less than 0.7 nm [1].

Elemental analyses for C and H content were performed by Exygen Research (State College, PA). The skeletal density of the carbons was measured on an AccuPyc 1330 (Micromeritics, Norcross, GA).

3. Results

Sample names correspond to their maximum temperature, for example PFA300 was pyrolyzed at 300 °C. PFA25 was reacted for a time sufficient at room temperature to induce cross-linking and solidify prior to analysis.

Fig. 1 shows the weight loss versus pyrolysis temperature of PFA along with its derivative. A major weight loss at 100 °C corresponded to evaporation of water, which was formed as a by-product of the polymerization reaction. As
the conversion of the polymer to carbon began, weight loss occurred in two distinct temperature regimes and gaseous by-products of the decomposition were determined by mass spectrometry, see Fig. 2. In the region of 300–400 °C the by-products were primarily H₂O and CO. A second major weight loss occurred between 400 and 600 °C. The production of CO increased, while H₂O was slightly suppressed. Generation of CH₄ and CO₂ was initiated in this region.

Infrared spectra of PFA were collected as a function of pyrolysis temperature and are shown in Fig. 3. The main characteristic peaks for PFA25 were at 3400 cm⁻¹ (OH stretch), 3100 cm⁻¹ (CH in aromatic rings), 2970, 2920 and 2850 cm⁻¹ (aliphatic CH₂ and CH stretch), 1600 cm⁻¹ (C=C aromatic), 1550 and 1500 cm⁻¹ (ring vibrations), 1460 cm⁻¹ (asymmetric CH₂ bending), 1350 cm⁻¹ (CH ring deformation), 1100 cm⁻¹ (C=O stretch), 1010 cm⁻¹ (OH) and 760 cm⁻¹ (2,5-di-substitution of furan ring). A peak at 1710 cm⁻¹ indicated carbonyl groups due to acid-catalyzed ring opening of furan rings. There was also evidence for the presence of CH₃ terminated groups at 1380 cm⁻¹, which signals the formation of conjugated sequences on the polymer backbone, as shown by Choura et al. [15]. As we increase the pyrolysis temperature to 200 °C, we found that many of the characteristic peaks of PFA were still present. The main differences were seen in the region of CH₂ and CH stretches; 1350 cm⁻¹ had shifted to 1400 and 1620 cm⁻¹ (C=C aromatic) appeared.

The infrared spectrum of PFA300 exhibited new signals, which were unique to carbon, along with the remnants of the polymer. The disappearance of the peaks at 1050 and 1100 cm⁻¹ indicated a complete rupture of the ether linkages, while polyaromatic signals appeared at 1200, 1145 and 1065 cm⁻¹, and the peak at 1620 cm⁻¹ broadened. The OH groups were still present at 3400 cm⁻¹, but peaks due to furan ring vibrations waned. A new peak arose at 1750 cm⁻¹ suggesting the presence of additional carbonyl groups. The spectrum of PFA400 demonstrated the continuing conversion of polymer to carbon. Strong vibrations due to CH rocking appeared at 960, 850 and 790 cm⁻¹, respectively. Polyaromatic signatures dominated the PFA500 spectrum.

Detailed structural information was obtained from solid state ¹³C NMR; the results are given in Fig. 4. Several structural models of PFA and its carbon, with specific moieties marked, are shown in Fig. 5. The characteristic
chemical shifts of PFA25 are approximately 25, 110, and 155 ppm. These resonances correspond to —CH2 groups linking furan rings on the polymer backbone (labeled A), carbon atoms at the 3 and 4 positions on the furan ring (labeled D), and carbon atoms at the 2 and 5 positions on the furan ring (labeled C), respectively. The assignments were in agreement with those published by Chuang et al. [16]. Two additional peaks were notable in the samples. The broad peaks at ~95 and ~130 ppm were attributed to conjugated sequences in the polymer (labeled B). A by-product of the conjugation reaction is —CH3 terminated PFA (labeled E), which was found in the spectrum at 15 ppm. The signature of cross-linked structures was identified as the broad peak at 45 ppm, which corresponded to —CH groups at the two possible cross-link junctions (labeled F). PFA100 was similar to PFA25, expect for a reduction in the peak at 145 ppm, which signaled the carbon at the α-position on a terminal furan ring. This disappearance marked the extended polymerization of the PFA. Residual THF appeared at 68 ppm in both PFA25 and PFA100. After heating to 200 °C the indicators of conjugation were intensified at ~95 and ~130 ppm. A continued presence of cross-links was indicated by the broad peak at ~45 ppm. Hydrolyzed furan rings appeared in the spectrum at ~200 ppm for samples PFA25, PFA100, and PFA200.

The broad peak at ~130 ppm grew substantially in the sample PFA300. It now represented both conjugated species and sp2 hybridized carbon in polyaromatic domains (labeled G). All peaks representing polymer moieties were maintained at 300 °C. The spectrum of PFA400 was dominated by polyaromatics. The peaks assigned to conjugation and cross-linking were absent, yet a signal for —CH3 groups remained at 15 ppm.

The cumulative pore volume and pore size distribution of the carbons, as measured by methyl chloride adsorption, are given in Fig. 6. PFA200 was essentially non-porous. It is interesting to note that as the temperature was increased to 300 °C, there was spontaneous generation of both micro- and mesopores in PFA300. The porosity of PFA400 was similar. When the temperature was raised to 500 °C, many of the carbon’s mesopores collapsed, while the micropore volume increased. At 600 °C the microporosity was unchanged and the mesopores had completely disappeared. The micropores were relatively monodisperse in size and centered at 4–5 Å.

High-resolution C 1s spectra of each PFA are overlaid and given in Fig. 7. The full widths at half max (FWHM) of the main peak corresponding to C—C or C—H are shown in Table 1 and decrease with increasing temperature. The line shape for PFA200 was very broad and almost Gaussian; this is typical for polymeric materials. There was a substantial amount of oxygen moieties in this material, the O/C ratio is ~0.28. This was reflected in the C 1s line shape as shoulder peaks at higher binding energies (286–288 eV). The O/C ratio dropped as the pyrolysis temperature increased to 300 °C (O/C ~0.16) and continued to decrease gradually. The shoulder peaks in the C 1s spectra also decreased with increasing temperature. The main peak
FWHM decreased and the line shape became highly asymmetric with increasing temperature. This was indicative of the increasing polyaromatic nature of the material. The FWHM nearly became less than 1, when the pyrolysis temperature exceeded 500 °C.

Table 1 also summarizes the elemental composition and skeletal density of the samples pyrolyzed at different temperatures. The H/C ratio in the sample is 1.0 at room temperature. As we increased the temperature, the H/C gradually started to decrease. It is interesting to note that a significant amount of hydrogen remained in the sample pyrolyzed up to 500 °C (H/C < 0.42). However, the H/C ratio dropped drastically between 500 and 600 °C. The densities of the samples were relatively constant over the temperature range of interest.

The thermal history of the carbons was probed by continuing the pyrolysis in the TGA up to 800 °C. The results are given in Fig. 8. PFA200 began losing weight at ~200 °C. Both PFA300 and PFA400 were stable until ~400 °C, at which point PFA300 began to lose weight more rapidly. The profiles of PFA500 and PFA600 were similar until ~500 °C and their weight loss was much less than that of PFA400. A sample was also pyrolyzed at 300 °C with a two week soak time. The continued pyrolysis of this sample is given in Fig. 9 and is compared to PFA300, PFA400, and PFA500. The weight loss during continued pyrolysis for the two week sample was less than that observed for PFA300 and PFA400. The two week profile is identical to PFA400 above ~500 °C. Decomposition reactions which occurred within one hour at 400 °C were induced at 300 °C by thermal soaking for extended time. Pyrolysis reactions requiring temperatures in excess of 400 °C did not occur at 300 °C.

4. Discussion

Inherent meso- and microporosity make NPC derived from PFA an attractive candidate for numerous technologies, yet the processes required to generate these properties remain poorly understood at the molecular level. The pyrolysis of PFA has been extensively characterized at several temperatures during its thermal history. These observations have provided insight to the dramatic chemical and physical changes which occur as PFA is transformed to NPC.

At 25 °C the polymer PFA is primarily comprised of furan rings linked together by methylene (–CH2–) bridges. According to Choura et al., cross-linking in PFA is predicated upon the formation of conjugated sequences on the polymer backbone [15]. Evidence of both conjugated and cross-linked structures has been found in the IR and NMR spectra of PFA200. Conjugation creates a double bond between the β carbons of the furan ring (labeled B), which results in a shift of the 1350 cm\(^{-1}\) –CH stretch to 1400 cm\(^{-1}\) and the appearance of the 1620 cm\(^{-1}\) signal in IR spectrum. The broad peaks in the NMR spectrum at ~95 and ~130 ppm, which intensify between PFA25 and PFA200, are attributed to conjugated sequences in the polymer. A second indicator of conjugation is the peak at ~15 ppm representing –CH3 terminated PFA chains, which are a by-product of the conjugation reaction. Cross-links are signified by the broad peak at ~45 ppm, which corresponds to –CH groups at the cross-link junctions (labeled F). The cross-links are a result of either a methylene bridge or Diels–Alder condensation.
Increasing the pyrolysis temperature to 300 °C induces the spontaneous generation of micropores. Surprisingly, a significant amount of mesoporosity is also developed in PFA300. Loss of the IR signals at 1050 and 1100 cm\(^{-1}\) and evolution of CO and CO\(_2\) in the mass spectrum confirm a rupture of the furan ring ether linkages. The O/C ratio drops precipitously from 0.27 to 0.16. Furan ring vibrations disappear from the IR as the fractured rings coalesce to form polyaromatics (labeled G in Fig. 5), whose presence is shown by the IR peaks at 1200, 1145 and 1065 cm\(^{-1}\). The broadened signal in the region of 1620 cm\(^{-1}\) now represents both polyaromatics and the remnants of polymer conjugation. The polyaromatics also appear in the NMR spectrum at 1-130 ppm. Incomplete scission of the ether linkages leads to carbonyl groups on the residual polymer, typified by the new peaks at 1710 and 1750 cm\(^{-1}\) in the IR (labeled H). A number of oxygen moieties are also expected to reside on the polyaromatic domains (labeled H), as in activated carbon samples. There is very little change in the H/C ratio between PFA200 and PFA300; therefore the carbon must also be infused with residual hydrogen from the furan rings and methylene bridges.

At 400 °C the hydrogen content is reduced, due to the release of CH\(_4\). The IR spectrum exhibits strengthened polyaromatic signatures at 1620, 1200, 1145 and 1065 cm\(^{-1}\). The carbonyl peaks are maintained in the IR at 1710 and 1750 cm\(^{-1}\). In addition, the micro- and mesoporosity of PFA400 is similar to PFA300. Fig. 8 demonstrates that when pyrolysis is continued in the TGA, PFA300 and PFA400 behave identically until heated to greater than 400 °C. Therefore heating the sample to 400 °C has not induced significant further decomposition of the residual polymer and heteroatoms in the sample.

The second major weight loss occurs when the PFA is heated to 500 °C. The H/C and O/C ratios are further reduced by the release of CO, CO\(_2\), CH\(_4\), and H\(_2\)O. The chemical changes are accompanied by a radical change in the porosity. Surprisingly, the mesopore volume is significantly reduced. The loss of mesoporosity correlates with the elimination of carbonyl groups in the IR spectrum and reduction in hydrogen content. The post-pyrolysis TGA profile of PFA500 is more similar to PFA600 than PFA400. Much of the decomposition that will happen by 600 °C has already occurred at 500 °C.

Extensive characterization of the PFA in the temperature range of 200–600 °C allows us to address the mechanism of micro- and mesopore formation in the carbon. The ether linkages in the furan rings fracture at 300 °C, leading to liberation of oxygen in the form of CO and CO\(_2\) gases. Remnants of the furan rings coalesce to form highly disordered aromatic domains within which the micropores reside. At this temperature the pyrolysis is incomplete, leaving partially fractured ether linkages to form carbonyl groups among the aromatics. These fragments more closely resemble the original polymer, rather than the final carbon, and are the cause of mesoporosity. A large fraction of the hydrogen species present in the original polymer also remain in the material. The polymer fragments and the oxygen (hetero) atoms buffer the aromatic domains from one another, creating the void spaces, or mesopores, in the material. The TGA profile of PFA soaked at 300 °C for 2 weeks is similar to PFA400, which was soaked for 1 h. Although decomposition continued over the two-week period, the pore size distribution was identical to PFA300. Very little change in porosity occurs at 400 °C; rather the existing aromatic domains are annealed, leading to stronger IR signals. A thermal barrier to continued pyrolysis exists at 400 °C. When this obstacle is defeated by heating to 500 °C a second major weight loss is seen as the polymer remnants are decomposed and oxygen (hetero) atoms are ejected, creating increased microporosity. A consequence is the loss of mesopores, which now collapse without the buffering polymeric material. The few remaining mesopores are mostly eliminated by heating to 600 °C; this effect is again accompanied by a slight increase in micropore volume.

5. Conclusions

Fitzer and Schafer suspected open pores with diameters smaller than 100 Å must be present to facilitate the transport of gaseous products formed during the pyrolysis PFA [5,6]. This hypothesis has been confirmed and a clear picture of the intermediates formed during pyrolysis is now available. Upon heating to 300 °C, PFA spontaneously decomposes and begins to convert to a mesoporous solid consisting of polymer remnants and aromatic cores that form the basis for the NPC which is produced with further pyrolysis at higher temperature. Oxygen and hydrogen moieties decorate the aromatic domains and the residual polymer in the material and thereby create the transient mesopores. The heteroatoms are driven out by heating above 400 °C and the mesopores then collapse. A carbon characterized by monodisperse micropores remains at 600 °C.

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