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Micro-FTIR and micro-Raman studies of a carbon film prepared from furfuryl alcohol polymerization

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The synthesis of a carbon film by the acid-catalyzed polymerization and resinification of furfuryl alcohol with a diluted solution of HCl is studied by combining micro-FTIR and micro-Raman spectroscopies. The detailed study of the evolution of spectra as a function of dosage of furfuryl alcohol and temperature shows that neutral and protonated species are formed at 80°C, while upon gradually increasing the temperature up to 600°C, the viscous polyfurfuryl alcohol resin is transformed into a carbon phase, containing a heterogeneous distribution of pores, with a size in the 100-2000 nm range, as shown by SEM and AFM analyses.

It is well-known that carbonaceous materials derived from the pyrolysis of furfuryl alcohol (FA) have a wide range of applications in the production of gas separation membranes, electrode materials, acid-resistant materials, corrosion inhibitors, and the binding phase in cement.¹⁻⁵ The acid-catalyzed oligomerization and resinification processes have been studied intensively in the past, and in general terms, the features of the processes are understood.⁶⁻⁹ The most widely accepted mechanism is the formation of conjugated sequences in the polymer chains, associated with the formation of colored species.⁶ The acid-catalyzed reaction of two furfuryl alcohol molecule initially produces a colorless bis(furyl)methyl group, as reported in structure I in Scheme 1. Following Scheme 1, these oligomers undergo hydride ion exchanges from the carbon atom joining two furan rings with the carbenium ion, formed by water elimination from a protonated methylol termination of another polymer. It must be emphasized that the first, second, third, and so forth formed methyl groups are accompanied by the formation of carbenium ions containing two, three, four, and so forth conjugated rings in positively charged oligomeric species. The reaction leading to colored species is not the only one occurring during the process; in fact, the formation of α,β -diketone structures, via the furan ring opening, has been suggested too⁸ (Scheme 2). When the monomer is mixed with an acid catalyst, a highly exothermic reaction occurs, which gives rise to the formation of oligomers with an intense brown color, which turn to black resins as the reaction reaches its end. Furthermore, at a later stage of the polymerization process, the polymer growth is characterized by the formation of branched species of the insulating resin, whose study is made particularly difficult by the insolubility of the products.^{9,10} The structure of the resin depends on the experimental conditions, such as temperature, solvent, and concentration of the acid mainly. When the viscous

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(and colored) product is subjected to thermal treatment in a flow of inert gas, by gradually increasing the temperature up to 1000 °C, the material becomes rigid and black due to the process of carbonization, leading finally to the formation of amorphous carbon. The acid-catalyzed FA polymerization by hydrochloric acid (HCl) has not been yet studied extensively. It has been reported that when the monomer is exposed to the vapors of a highly concentrated HCl solution, a highly exothermic reaction occurs, which gives rise to the formation of oligomer clusters, which bind each other to generate a porous and electrically conductive pellicle.^{11,12} In more detail, there are three critical temperatures for the pyrolytic process of carbonaceous materials,¹³ the carbonization temperature at about 400 °C, when the molecular structure of polyfurfuryl alcohol (PFA) is degraded and carbonization begins; the nucleation temperature at 550 °C, when a large number of small graphitic crystalline nuclei are formed; and the crystallite growth temperature at 700 °C, when the nuclei grow and large crystalline grains are observed. The size of the microcrystallites increases quickly by increasing the temperature as well as by increasing heating treatment time. In the present work, we report a combined study of vibrational properties and surface morphology of a carbon film, obtained from polymerization of FA with HCl and pyrolyzed from 100 to 600 °C. PFA resin was prepared by stirring a diluted solution of HCl [HCl/H₂O, 1/3] in FA at 80 °C for 10 min. The resulting viscous PFA resin was then activated at 100, 200, 300, 400, 500, and 600 °C under Ar gas flow (100 mL/min). In order to control the polymerization mechanism and the structure of the carbon phase, the as-prepared samples were characterized after each thermal treatment by means of Fourier transform infrared microspectroscopy (AutoImage micro-FTIR microscope system, Perkin-Elmer, with a 4 cm⁻¹ resolution and an area of analysis of 100 × 100 μm²), micro-Raman (Renishaw in Via Raman Microscope with a 50× objective and a He-Cd laser emitting at 442 nm), scanning electron microscopy (Leica Cambridge Stereoscan 420 instrument equipped with an energy dispersive X-ray spectroscopy), and atomic force microscopy (Park Scientific Instrument Auto Probe LS). Figure 1 shows micro-FTIR spectra of FA polymerization with HCl after thermal treatment, under Ar gas flow at 100, 200, 300, 400, 500, and 600 °C (curves b-g). Curve (a) reports the spectrum obtained after stirring FA with a diluted solution of HCl at 80 °C, while the gray spectrum corresponds to liquid FA at 25 °C.

In a previous work, a similar sequence of FTIR spectra for FA adsorbed on H-Y zeolite at temperatures ranging from 25 up to 400 °C has been obtained in order to understand whether longer oligomers can be formed under different conditions by imposing a constraint on the growth of the oligomeric chains.¹⁴ This is in line with previous works concerning the polymerization of unsaturated hydrocarbons within zeolitic frameworks.¹⁵ From Figure 1, it is clearly evident that the as-prepared sample (curve a) still shows the spectral features of liquid FA (gray line, astericks on curve a). The band at 1715 cm⁻¹ can be assigned to the stretching vibration of carbonyl species, thus supporting the hypothesis of the formation of diketonic structures.⁸ The absorption observed at 1565 cm⁻¹ could be ascribed to (C=C) modes of neutral or cationic polyunsaturated species.¹⁴ This last assignment could support the coexistence of both neutral conjugated species, formed by FA polycondensation, and the cationic species derived from protonation with HCl. We shall return to this point in the following when we illustrate the Raman results. After heat treatments at 100-200 °C, the absorptions at 1675 and 1422 cm⁻¹, ascribed to the ring stretching modes of the 2-substituted and 2,3-disubstituted furan rings of PFA, and the components at 1215-1180 and ~1015 cm⁻¹, assigned to

the asymmetric and symmetric stretching vibration of =C–O–C groups belonging to 2-substituted furan rings,¹⁶ significantly grow. These last assignments support the formation of branched polymeric species. From this sequence of spectra, it comes out that the formation of polymerized PFA occurs already at 100 °C (curve b), and it seems to be complete at 200 °C (curve c). On the sample treated at 300-500 °C (curves d-f), all of the absorptions in the 1675-1015 cm⁻¹ range disappear, and the component at 1715 cm⁻¹ significantly decreases in intensity. At the same time, two main broader bands grow at ~1600 and ~1300 cm⁻¹, which become predominant after thermal treatment at 600 °C (curve g). On the basis of the literature data concerning amorphous carbon and carbon nanotubes,^{17,18} absorptions at ~1600 and ~1300 cm⁻¹ indicate the formation of the carbonaceous material.

In order to investigate the nature of the formed carbonaceous species, two types of experiments have been performed by means of the micro-Raman technique. First, we obtained the spectra under the local heating effect of the laser beam, in particular, the spectra of liquid FA (Figure 2, gray line) and that of the FA/diluted HCl solution (Figure 2, curve a). Then, the spectrum of the viscous PFA resin after thermal treatment at 600 °C, under Ar gas flow, was recorded (Figure. 2, curve b). Furthermore the exciting line at () 442 nm (22624 cm⁻¹) is expected to cause Raman resonant effects on species adsorbing in the visible region, where both neutral and cationic conjugated species absorb;^{6,14} consequently, we expect that the Raman spectra are dominated by the vibrational manifestations of them.

From Figure 2, it is clearly observable that the spectrum of the FA/diluted HCl solution (curve a) shows still the spectral features of liquid FA (gray line, astericks on curve a); they can be assigned to the vibrational modes of PFA chains. On the contrary, the peaks at ~1650, ~1560, and ~1522 cm⁻¹ can be attributed to cationic unsaturated moieties, which derive from protonation by HCl and are inserted into the polymeric chains.¹⁴ From this, it can be argued that the infrared band at 1565 cm⁻¹ is due to carbocationic oligomeric species (Figure 1). The contemporary presence of all of these features reveals the coexistence of both cationic and neutral (carbon-type) species. This implies that the micro-Raman spectrum of samples, obtained under the laser beam by adding a diluted HCl solution to liquid FA at 25 °C, can be compared to the micro-FTIR one, even if recorded on samples prepared after stirring FA with a diluted solution of HCl at 80 °C (Figure 1, curve a). In fact, it can be considered that there are both thermal and photoactivation effects of the laser beam on the samples.

When the so-obtained sample is treated at 600 °C under Ar gas flow (curve b), all of the features ascribed to oligomeric and cationic species disappear, while two broader Raman absorptions centered at ~1600 and ~1350 cm⁻¹ (G and D peaks, respectively) grow. From the position and the shape of these components, the complete transformation of the FA polymer into a turbostratic carbon phase can be further highlighted.^{9,13,19,20} Figure 3 shows SEM and AFM images of the morphology of the carbon material treated at 600 °C. In particular, from the SEM analysis (Figure 3a), the presence of a heterogeneous distribution of holes with sizes in the 500-2000 nm range is clearly evidenced. Furthermore, from AFM images, holes with smaller diameters in the 100-300 nm range are very clearly imaged (Figure 3b). In a previous work from us,²¹ a porous carbon surface was produced after thermal treatment at 800 °C of ZnO-carbon composites, which was obtained from a homogeneous mixtures of FA with ZnCl₂. In that case, the ZnCl₂ catalyst was acting as a templating agent for the production of pores, whose distribution and diameters depend on the Zn concentration. In fact, the carbon phase gradually changes from a homogeneous distribution of holes (less than 1 μm in size) (low Zn concentration, 4.8% w/w) to a more disordered situation (high Zn concentration, 17% w/w), with wide pockets and small cavities simultaneously present

(200-500 nm in size).²¹ On this basis, we can highlight the role of the catalyst in affecting the distribution and size of holes inside of the porous carbon phase. In previous studies, advanced analytical techniques have been used in order to characterize carbonaceous materials.²² In particular, structural studies using X-ray have demonstrated the relationships of the starting structure to the final graphitizability. Figure 3c reports an AFM image obtained in a region free from pores, which clearly shows the structure of the carbon phase, characterized by a surface average roughness of about 2 nm with a mean height of about 9 nm. The values reported were obtained from the region analysis within the selected area, which allows estimation of the distribution of heights (histogram plots, not reported for the sake of brevity). In conclusion, the synthesis of a carbon film by the resinification/ pyrolysis processes of HCl-catalyzed FA has been investigated by means of micro-FTIR/Raman techniques. The studies successfully show that neutral and protonated species are formed at low temperature (~80 °C), leading to the formation of solidified PFA already at 100 °C, whereas the amorphous carbon phase becomes dominating at high temperature of treatment (~500-600 °C). Furthermore, from SEM and AFM images on samples treated at 600 °C, a turbostratic carbon phase characterized by a heterogeneous distribution of pores is highlighted.

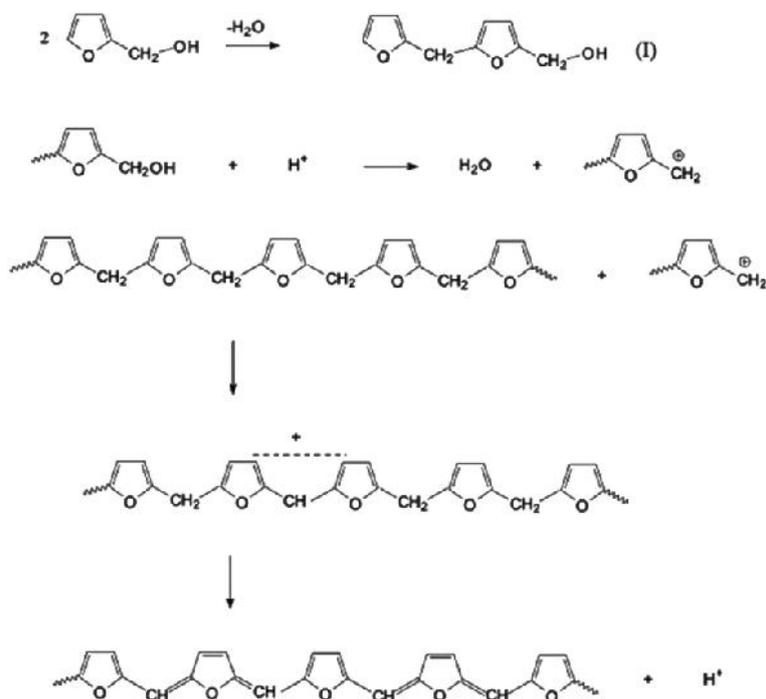
Acknowledgements

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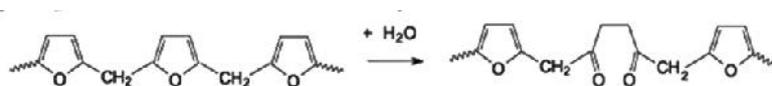
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Schemes and Figures and Captions



Scheme 1. Formation Reaction of Conjugated Sequences in the Polymer Chains



Scheme 2. Ring-Opening Reaction with the Formation of -Diketone Structures

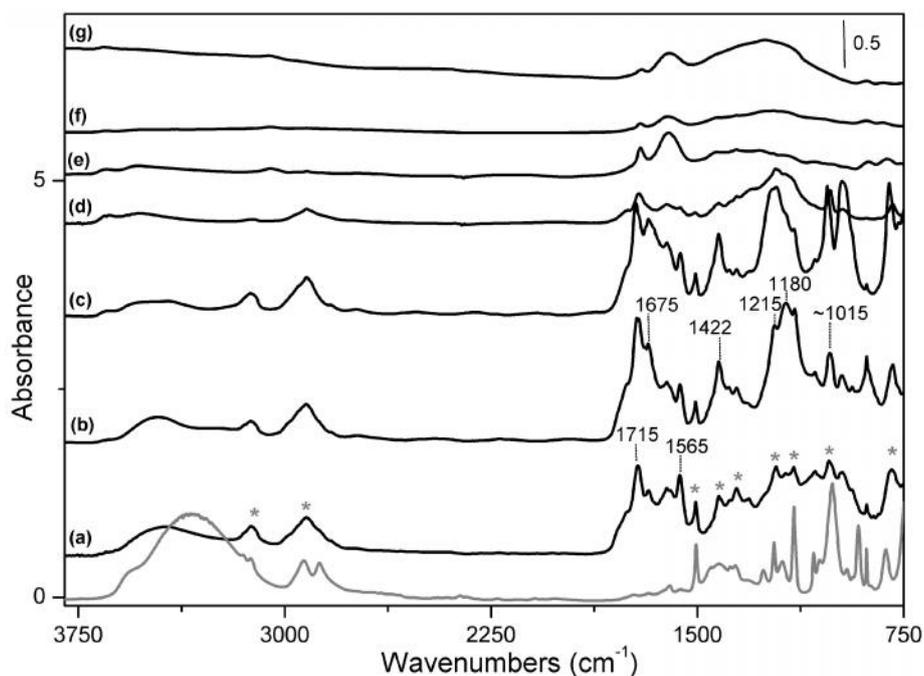


Fig. 1. Micro-FTIR spectra of the viscous PFA resin as prepared after stirring FA with a diluted solution of HCl at 80°C (a) and after activation at 100°C (b), 200°C (c), 300°C (d), 400°C (e), 500°C (f) and 600°C (g) under Ar gas flow. Gray line reports the spectrum of liquid FA at 25°C.

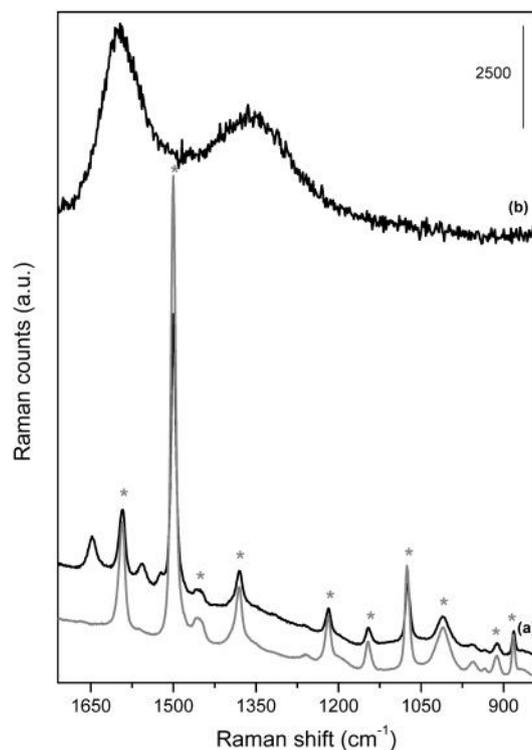


Fig. 2. Micro-Raman spectra of the FA and diluted HCl solution at 25°C (a) and of the viscous PFA resin after activation at 600°C under Ar gas flow (b). Gray line reports the spectrum of liquid FA at 25°C.

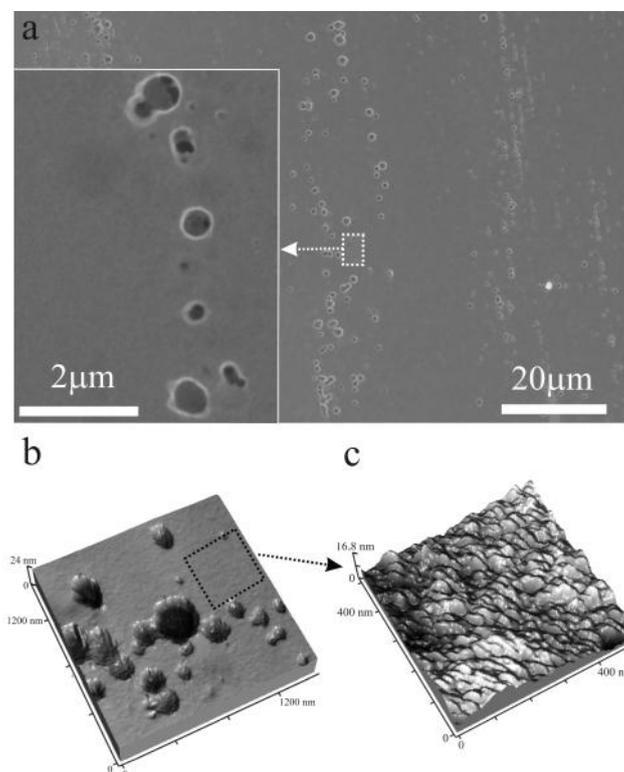


Fig. 3. (a) SEM image of the carbon material treated at 600°C: in the insert SEM enlarged view of a selected area in (a); (b) CM-AFM images of the carbon surface (1400 X 1400) nm and (c) CM-AFM enlarged view, (500 X 500) nm in size.