ZNO-CARBON COMPOSITES AND IMPRINTED CARBON MATERIALS VIA PYROLYSIS OF $ZNCL_2$-CATALYZED FURFURYL ALCOHOL POLYMERS

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Abstract

The sequential synthesis of C/ZnO composites and imprinted porous-C materials, from mixtures of $ZnCl_2$ and furfuryl alcohol (FA) precursors, is reported. Acting as a Lewis acid catalyst, $ZnCl_2$ promotes the polymerization of FA at 60-70°C. Upon temperature increasing (100-600°C, N_2+O_2 ppm) FA polymers pyrolyze, but Zn (II) species remain in the matrix. As a result, the material obtained at 600 °C becomes fully covered by an uniform film of ZnO microcrystals that are implanted on the carbonaceous matrix. The surface of the underlying C-support is characterized by the presence of holes, whose size and shape are related to those of ZnO microcrystals. Further heating treatments at higher temperature (600-800°C, N_2+O_2 ppm), lead to an imprinted C-material, where ZnO phase disappeared after reacting with the C-phase. The materials, obtained by pyrolysis process, have been investigated by TPD, FTIR, SEM, AFM, XRD and Raman. The effect of $ZnCl_2$ concentration on the process of ZnO and C-phase formation, has been studied in detail.

Introduction

Porous carbons are usually prepared by pyrolysis of polymers. Polyacrylonitrile (PAN), phenolic resin, polyimides, poly(p-phenylene vinylene), polyvinyl acetate and polyfurfuryl alcohol (PFA) are some of the most commonly used precursors [Pierson, 1993]. Among them, PFA (obtained by acid catalyzed polymerization of the monomer) provides a relatively high carbon yield (50-55%) [Pierson, 1993] and gives rise to amorphous carbons that are caracterized by the presence of defects along the graphene sheets, such as pentagons, heptagons, vacancies, impurities and other non-hexagonal rings [Petkov, DiFrancesco, 1999, Strano, Zydney, 2002, Zarbin, Bertholdo, 2002]. The amorphous carbons retain their structures up to very high treatment temperatures (2500-3000°C) before to be converted into graphitic structures.

The polymerization of furfuryl alcohol (FA) is acid-catalyzed. Catalytic systems commonly reported in literature are:

(i) mineral (H_2SO_4, etc.) and organic (p-toluenesulphonic, etc)acids [Pierson, 1993, Principe, 1999, Vergunst, 2002],
(ii) acid zeolites (HY, HZSM-5) [Rodriguez-Mirasol, 1998, Sthel, 1999]
(iii) Lewis acids ($SnCl_4$, $TiCl_4$) [Gonzalez, 2002].

In this work, we have investigated the catalytic effect of a Lewis acid ($ZnCl_2$) on the polymerization of FA and the fate of the catalysts dispersed in the polymeric matrix upon thermal treatments in the 70-800 °C interval under N_2 (O_2 ppm) atmosphere treatment.

Methods

PFA resins have been obtained by dissolving 5% w/w of $ZnCl_2$ in liquid FA at room temperature. By stirring the mixture under mild conditions (80°C) a rapid polymerization of FA with subsequent formation of a brown, highly viscous, phase of PFA is observed. During this stage, $ZnCl_2$ (or its hydrolysis products) remains dispersed into the polymeric matrix. Pyrolysis treatment have been performed under 100 ml/min N_2 + O_2 ppm gas flow at 200°C, 400°C, 600°C and 800°C.

Samples, coming from the different temperature treatments, have been characterized by means of: FTIR spectroscopy (Perkin-Elmer Spectrum Spotlight 300 FTIR microscope), SEM microscopy (Leica Cambridge Stereoscan 420), AFM microscopy (Park Scientific Instrument Auto Probe LS), Raman spectroscopy *(Renishaw in Via Raman Microscope spectrometer* emitting at 514), XRD analysis (Philips PW3020 diffractometer, Cu $_{Ka}$ radiation in a standard Bragg–Brentano geometry). TPD analysis (Hyden Catlab) have been performed on PFA obtained after polymerization upon thermal treatment at 70°C.

Results and discussion

In the last decades many efforts have been devoted to understand the acid-catalyzed polymerization of furfuryl alcohol. It is known that the general mechanisms of the polymerization can be summarized as follows:

i) reaction occurring between -CH_2OH groups and C-H of two adiacent FA molecules to form CH_2-linked furan rings (olygomerization) [Dunlop and Peters, 1953];
ii) reaction occurring between -CH_2OH groups of two adiacent FA molecules to form H_2C-O-CH_2-linked furan rings (condensation) [Dunlop and Peters, 1953];
iii) formation of conjugated chain species via-carbocation rearrangement of double bonds [Bertarione, 2007] (data not shown for sake of brevity), responsible for the polymer intense colouring [Choura, 1996].

We do not speculate anymore on the polymerization of FA, which is a complex process and cannot be limited only to a linear polymerization phenomenon occurring at 2,5-ring position. According to a such strict definition, many products could not be properly defined as PFA resins, because they could form other products, coming from side reactions simultaneously occurring with PFA formation.

The resulting viscous and coloured material contains not only randomly type i) and ii) chain sequences, whose double bonds can be redistributed to form conjugated species, but also chain sequences coming from furan ring opening [Conley and Metil, 1963] if treated at relatively high temperatures.

When the so-obtained resin is thermal treated by gradual temperature increasing (RT-800°C) under a flow of inert gas, the material becomes rigid and more dark coloured. Upon the pyrolysis process, volatile species are released. In Fig. 1 the TPD analysis is shown. In this figure two distinct regions are shown, where volatile species are released. In the first one (RT-250°C), water goes out from the polymer, which is still resinificating. At higher temperature (300-600°C), besides water other volatile species, are detected (CO, CO_2, CH_4, other hydrocarbons). After gas evolution upon pyrolysis, the formation of an amorphous carbon, is commonly accepted in literature [Foley, 1995, Pierson, 1993].

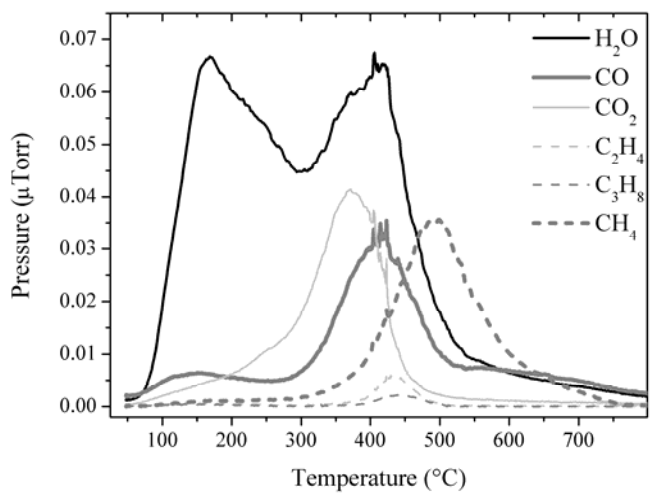


Figure 1. TPD analysis of PFA/Zn (II) composite, obtained from FA+ $ZnCl_2$ 5% w/w, under He gas flow in the RT-800°C temperature range.

A further support to of the carbon formation, comes from IR investigation of materials obtained at different stages of pyrolysis (70°C, 200 °C, 400 °C, 600 °C and 800°C) under N_2 (O_2 ppm) atmosphere, as shown in Fig. 2. In this figure, the progressive evolution of IR bands is reported. In particular, IR spectrum of sample polymerized at 70°C (curve b) is compared to that of liquid FA at RT (curve a). More in detail:
i) the broad absorption at 3402 cm^{-1} is related to the stretching mode of the -OH ending groups of the PFA polymer chains, even if adsorbed water can contribute to the total intensity. This band is weaker than that of pure FA, which has one –OH group every furan ring [Choura, 1996],
ii) the bands at 2923 and 1422 cm^{-1}, assigned to -CH stretching and -CH scissoring vibrational modes of aliphatic -CH_2 groups, are present in both cases,
iii) the bands at 1020, 1149 and 3125 cm^{-1}, assigned to C-O-C and C-H aromatic stretching modes, are the typical fingerprint of the furan ring present in FA and PFA,
iv) peaks at 793 cm^{-1}, related to 2,5-disubstituted furan rings [Choura, 1996], not found in IR spectrum of FA, is confirming the occurrence of the oligomerization process, whereas 2-monosubstituted furan heterocycles are present as well (band at 735 cm^{-1}) [Choura, 1996],
v) the broad band appearing at 1715 cm^{-1} in the IR spectrum of PFA, which has been assigned to C=O band, suggests a the occurrence of some ring-opening probably induced by the acidic medium [Choura, 1996], whose product has been ascribed to a polymer sequence containing the ester of levulinic acid [Sugama, 1985].

As far as the Zn species are concerned during the polymerization, their fate seems to be correlated with carboxylate anions species (COO^-), whose typical bands are at 1560 cm^{-1} and at 1420 cm^{-1}. The formed product of polymerization is well compatible with Zn-FA chelate coumpounds. [Sugama, 1985].

Sample treated at 200°C (curve c) shows a weaker IR spectrum. By considering the fingerprint modes previously assigned to PFA, the band at ~790 cm^{-1} becomes stronger and broader, hence we speculate that polymerization is going on with the 2,5-disubstitution of furan rings. It is worthy noticing that C=O stretching frequency of the polymer (1710 cm^{-1}) decreases upon hydrogen bond formation through the carbonyl oxigen [Sugama, 1985] and that $–CH_2$ and –CH bonds of the ring disappear at increasing temperature of treatment, in accordance with literature data [Wang, 1998].

IR spectrum of sample treated at 400°C (curve d) exhibits different features. Besides –OH and aliphatic $–CH_2$ vibrational modes (3515, 2921 and 1433 cm^{-1}, respectively), three broad bands appear with maxima at 1706, 1603, and 1220 cm^{-1}, respectively. The evolution of IR bands in the 1700-1500 cm^{-1} range is typical of C=C stretching modes of neutral and charged conjugated species of variable length. It it worthy noticing that the bands at 1020, 1149 and 3125 cm^{-1}, previously assigned to furan ring fingerprints, have disappeared. This means that at this temperature, even if FA fragments are still present, polymer chains coming from the furan ring opening, are formed and can rearrange to form aromatic C-C ring sequences.

IR spectrum of the sample treated at 600°C (curve e) shows an apparent oversimplification. As the –OH and aliphatic $–CH_2$ vibrational modes fully disappear, two new and very broad bands, at 1598 and 1250 cm^{-1}, are emerging. The first band is located very close to the E_{1u} band of graphite (1588 cm^{-1}) and it might have been covered by the long tail between 1750-1500 cm^{-1} interval [Wang, 1998]. The second very broad band (1250 cm^{-1}) is attributed to the CH in-plane deformation along C-aromatic domains [Wang, 1998]. This fact can be debated considering that the advancing pyrolysis can open polymer crosslinking, whose terminations form C-aromatic domains as soon as volatile species, containing eteroatoms (CO, CO_2) and small fragments (CH_4, hydrocarbons, *vide supra*), are released.

IR spectrum of samples treated at 800°C (curve f) is very weak and no information about the carbonization process can be argued.

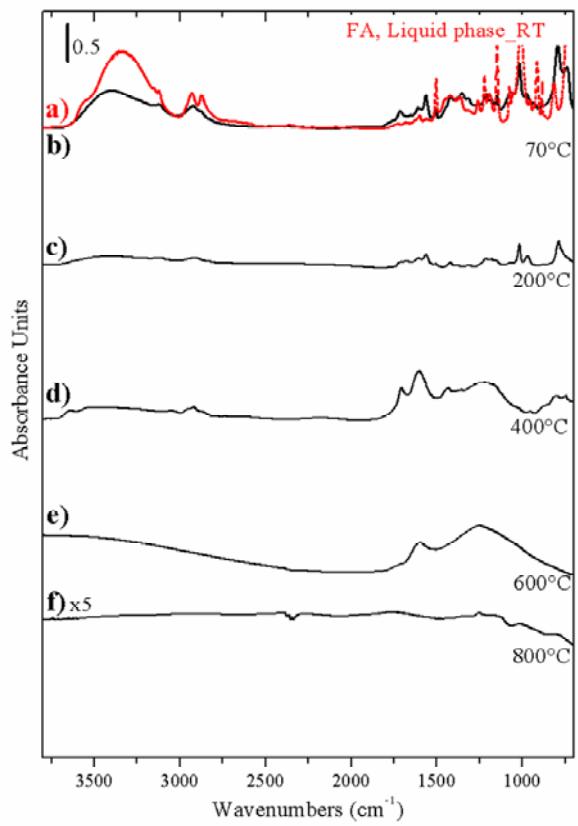


Figure 2. IR spectra of liquid FA (curve a), of sample polymerized at 70°C (curve b), and of samples treated under N_2 (O_2 ppm) atmosphere 200°C (curve c), 400°C (curve d), 600°C (curve e) and at 800°C (curve f), respectively.

Samples treated at 600°C and 800°C for 5h under N_2 (O_2 ppm) have been characterized by means of SEM, AFM, Raman and XRD analyses. SEM image of sample treated at 600°C is shown in Figure 3a. In this figure, a compact and homogeneous

layer of randomly oriented ZnO microcrystals lying on the carbon matrix is shown, whose terminations are imaged by AFM (Inset of Figure 3a). From this figure, regular extended prismatic and hexagonal faces are illustrated. The fact that cristals are formed by ZnO is confirmed from Raman and XRD analyses. In Figure 3b, Raman spectrum is reported. Besides the G (1580 cm^{-1}) and D (1350 cm^{-1}) bands, typical of an amorphous carbon with turbostratic structure [Robertson, 2002], also additional modes in the 600-300 cm^{-1} range are observed. The broad and weak features in the 600-500 cm^{-1} range can be assigned to E1 (LO) and A1 (LO) longitudinal phonon optical modes of ZnO, while the sharp peak at 436 cm^{-1} is related to the first order frequency of E2 mode [Calleja and Cardona, 1977]. Further support to the formation of a C/ZnO composite comes from XRD analysis. The XRD pattern of the sample obtained at 600°C reveals two broad diffraction peaks (maxima at 2θ = 24.5° and 43.3°) and five narrower peaks (at 2θ = 31.7°, 34.4°, 36.2°, 47.5° and 56.5°). The two broad peaks are assigned to the (002) and (100) diffraction planes of a turbostratic carbon phase [Johnson and Tison, 1969]. The narrow peaks are ascribed to the (100), (002), (101), (102) and (110) diffraction planes of wurzite ZnO phase. From the peak broadening and by using Sherrer's equation [Birks, 1946], the size of scattering coherent domains along the c-axis of the C-phase and along the (101) direction of the ZnO phase, have been found to be L_C=1.6 nm and ≈130 nm, respectively.

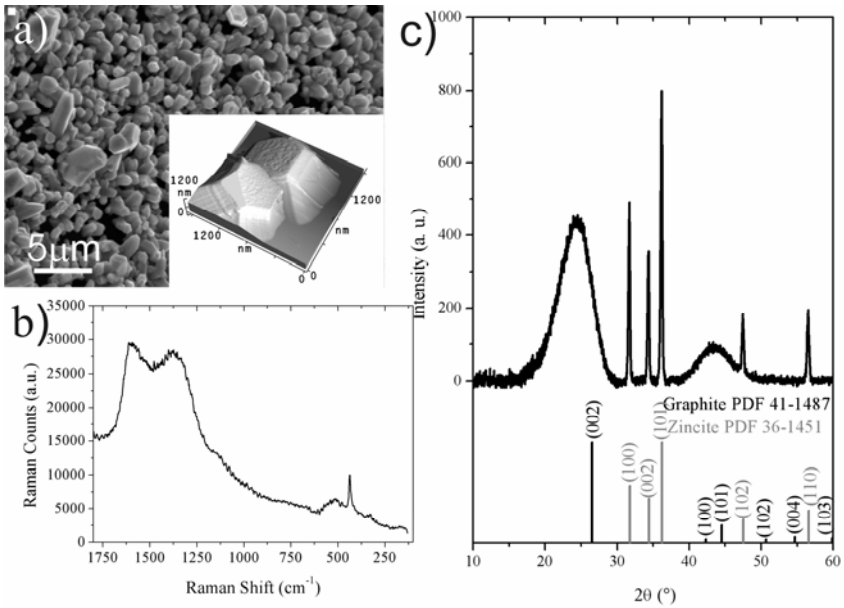


Figure 3. a) SEM/AFM, b) Raman and c) XRD analyses of sample obtained after thermal treatment at 600°C under N_2 (O_2 ppm) atmosphere.

SEM image of the sample treated at 800°C is shown in Fig. 4a. In this picture, the carbon phase surface clearly shows the presence of holes (inset in the upper part), whose topography is imaged by AFM (inset in the lower part). More insights on the occurring of the carbon phase come from Raman and XRD analyses. In Fig. 4b, Raman spectrum exhibits two broad bands at 1580 cm^{-1} and 1350 cm^{-1}, previously ascribed to G and D carbon bands of a non graphityzing carbon (turbostratic), formed under the adopted temperature of treatment [Robertson, 2002, Zerbi, 2006]. The XRD pattern of the sample obtained at 800°C reveals the two broad diffraction peaks (maxima at 2θ = 23.9° and 43.6°) related to (002) and (101) diffraction planes of the carbon phase. Note that the full with at half maximum (FWHM) of XRD diffraction bands remains very similar to those of C-phase of C/ZnO composite. This fact can be accounted for the structural order of such C-materials that becomes graphitic only at very high temperature (2500-3000°C) [Pierson, 1993].

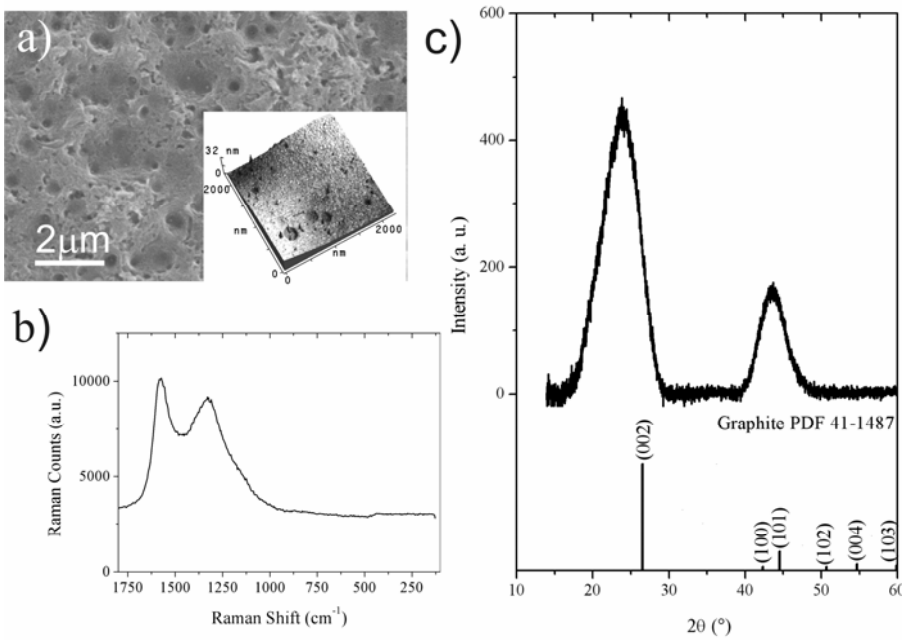
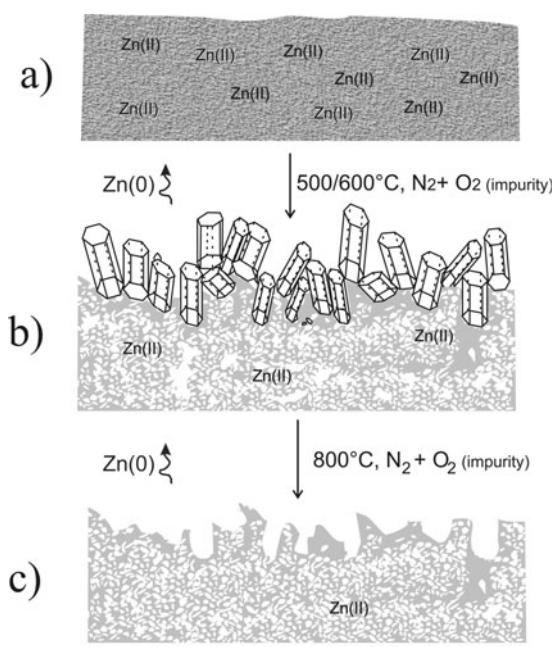


Figure 4. a) SEM/AFM, b) Raman and c) XRD analyses of sample obtained after thermal treatment at 800°C under N_2 (O_2 ppm) atmosphere.

An explanation of the process, can be proposed in Scheme 1. Zn(II)/PFA composite is plausibly the main product of polymerization a), which pyrolyzes upon increasing thermal treatment to form an amorphous carbon covered by a homogeneous film of ZnO microcrystals at 600°C implanted in the carbon phase b). The development of the ZnO phase can be ascribed to the presence of vapours of metal Zn (at T≥ ≈500°C) coming from the bulk material, where reduction processes take place (carbon phase is forming). As soon as metal Zn meets the external flow, which contains O_2 as impurity, is immediately oxidized to ZnO. When the temperature is higher enough, ZnO phase can be reduced againto Zn (0), which goes out from the surface leaving a holed C-surface c), which remembers the presence of the ZnO crystals before formed. We do not exclude that the size of the holes is also partially determined by the consumption of the carbon in direct contact with the ZnO particles.

Further support to the effects of the $ZnCl_2$ on the morphology and on the porosity have been reported [Cesano, 2007], but here not shown for sake of brevity.



Scheme 1. Schematic representation of main products obtained from the process of FA polymerization $ZnCl_2$ acid-catalized and then pyrolysis : PFA/Zn(II) composite a), C/ZnO composite (500°C) b), C-porous material, with imprinted surface c).

Conclusions

The process of polymerization and carbonization of a $ZnCl_2$/FA mixture has been studied in detail by means of several techniques (IR, TPD, SEM, AFM, Raman and XRD). The preparation of microporous carbons is obtained through several stages, leading to the initial formation of PFA/Zn(II) composite (through the action of the Zn^{2+} Lewis acid catalyst), carbon/ZnO composite and then to a pure porous carbon phase. For T < 400-500°C, Zn(II) remains dispersed in the carbonaceous matrix. For T≅500°C or more, metal Zn is formed and migrates at the surface of the carbon as vapour, where by contacting the O_2 impurities, film is formed which is characterized by ZnO microcrystals implanted in the carbon matrix.

At higher temperature (≈800°C), ZnO is reduced by the carbon phase and the formed Zn(0) leaves again the sample as vapour phase. As a result, a holed carbon phase is generated, whose surface has been imprinted by ZnO microcrystals previously present.

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