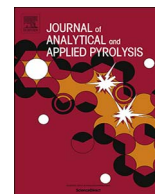




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## Reactive carbons from Kraft lignin pyrolysis: Stabilization of peroxy radicals at carbon/silica interface

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## ABSTRACT

Lignin, the most abundant aromatic natural polymer and the second richest source of organic raw material, is considered as a potential source of energy, chemicals and carbon-based materials. In this work we have investigated the nature and reactivity of  $sp^2$  carbons obtained by the pyrolysis of soluble Kraft lignin, a byproduct of paper making process. The formation of carbons from Kraft lignin deposited onto high surface area silica was studied by vacuum pyrolysis at different temperatures, using pristine and acid-washed lignin. Among the various techniques adopted for the material characterization, the Raman measurements showed that the procedure successfully yields carbon atoms organized in  $sp^2$  domains, on the surface of silica, whose dimensions are sub-micrometric. The identification of a very stable peroxy radical onto carbon-modified silica represents a major result, because these species are known to be usually transient. The observed peroxy radicals are detectable only when both pyrolytic carbon and silica are present. The reactions of pyrolytic carbon onto silica with oxygen and nitrogen monoxide were studied by electron paramagnetic resonance (EPR). The kinetics and reversibility of the reaction with oxygen, as well as the reaction with nitrogen monoxide, were investigated.

### 1. Introduction

Carbon is the most important element for life on Earth due to the role it plays in organic chemistry because of the flexibility of its bonding, and carbon-based systems show an unlimited number of different structures with a variety of physical properties [1]. Even if it is one of the elements known from the ancient times, up to recent years new carbon materials have been discovered and extensively studied for various applications, viz. fullerenes, nanotubes, graphenes and graphitic carbon nitride [2,3]. As it is well known, in one of its allotropic forms carbon is the hardest of the known materials, and in another one it is among the softest. Diamond is transparent, electrically insulator and very hard, contrary to graphite, that shows a blackish colour and is an electrically conductive, soft material. The change of hybridization from  $sp^3$  to  $sp^2$  induces a modification of the crystallographic structure from cubic to hexagonal. Besides these pure allotropic forms, if both hybridization states are present or if there is a low amount of other elements (especially oxygen) or a variable amount of defects (in particular free radicals and dangling bonds), a huge variety of

carbonaceous materials having properties in between can be produced.

Among the known carbonaceous solid materials, charcoal is the widest available and affordable. Charcoal is defined as the residue of solid non-agglomerated organic matter, of vegetable or animal origin, that results from thermal carbonization in the absence of air, at a temperature above 300 °C [4]. The physical properties of charcoal are unique, indeed the material can be a good (or poor) electrical conductor, it can show a high (or low) specific surface area, and it can have variable densities depending on the initial feedstock and the highest temperature employed in the carbonization procedure [5]. Charcoals and carbonized charcoals (biocarbons) and high-valued carbon nano-materials can be prepared from a wide variety of biomasses [6,7]; the structure of such carbons depends not only on the temperature of preparation but also on the nature of the starting material. For these materials, surface area, particle size, porosity, inorganic content, as well as temperature and degree of carbonization, are all important parameters for classification [8].

On the other hand, vegetal biomass contains variable amounts of lignin (LG), a complex three-dimensional polymer composed of

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phenylpropanoid units. It seems plausible that biocarbons derived from LG possess a graphite-like structure. Recent work reported that pyrolysis of lignocellulosic wastes is an easy, green route to prepare graphenes [9,10]. The LG base structure has in principle great potentiality to be rearranged in extended graphene-like aromatic layers, as demonstrated under microwave plasma irradiation [11] and also by pyrolytic treatment [12]. LG pyrolysis yields carbonaceous residues rich in polycyclic aromatic hydrocarbons [13,14], and polymeric carbon with fine sorption properties can be obtained from olive stones LG biomass [15]. It is also reported that softwood pyrolysis yields graphene sheets rearranged in turbostratic carbon [12]. LG can be considered as a waste material as it is the major by-product of second generation bio-ethanol production [16]. In particular, Kraft LG is obtained as a by-product of the paper pulping process. In the Kraft process the insoluble LG polymer present in wood is decomposed into smaller units under high temperatures (170–180 °C) in the presence of strong alkali solutions (sodium hydroxide) and sulfides. During the process the LG polymer backbone is broken and sulfides are included in the structure rendering it water soluble. The pyrolysis of LG, i.e. the treatment at high temperature in the absence of oxygen, leads to the elimination of sulfur and oxygen present in the polymer, thus leaving carbon as a residue. The LG backbone hydroxyphenylpropanoic units then can rearrange easily to give graphite-like extended aromatic structures. It is well known that the pyrolysis of Kraft LG proceeds in two steps according to the pyrolysis temperature. In the temperature range 200–400 °C carbon dioxide is produced together with volatile sulfur compounds [17], while in the range 500–600 °C carbon monoxide is evolved from phenols decomposition. Hydrogen gas production begins at 500 °C [18] indicating that, above this temperature, carbon defects are cured. The bulk pyrolysis of LG at high temperature (> about 3000 °C) is known to yield high-ordered carbon [19], and moreover supported carbons on inert inorganic materials can have very interesting properties and applications since they possess a conductivity by the sp<sup>2</sup> carbon sheets together with chemical reactivity and other relevant structural features; indeed inert supports (i.e. silica, hexagonal boron nitride, alumina and Si<sub>3</sub>N<sub>4</sub>) and pristine materials can be used for their preparation [20–24]. In this context, we showed that pyrolysis of Kraft LG deposited onto porous micrometric silica is an easy, effective route for silica surface modification with pyrolytic carbons [25]. A recent study described the free radicals in biochars from high temperature fast pyrolysis [26], but to the best of our knowledge the formation of radical species in the carbonaceous phase from pyrolysis of silica-supported LG has not been investigated.

In this work we deemed interesting and informative to study the nature and the reactivity of pyrolytic carbons generated on high surface area silica by using the vacuum pyrolysis technique. The pyrolytic carbons were extensively characterized by various techniques, that is Raman spectroscopy, electron paramagnetic resonance (EPR), thermogravimetric analysis (TGA) and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-IR). The reactivity of the carbon phase was investigated by reaction with oxygen and nitrogen monoxide. Interestingly, stable peroxide radicals obtained by reaction with atmospheric oxygen were observed and thus further investigated.

## 2. Materials and methods

### 2.1. Precipitated silica zeosil 1165

Precipitated silica Zeosil 1165 was purchased from Rhodia (Bollate, Italy) and used as received. Zeosil 1165 possesses a four level fractal hierarchical structure consisting of primary particles of ca. 10 nm forming particle aggregates of ca. 300 nm giving in turn hard agglomerates; the latter structure ultimately forms soft agglomerates of 100–200 µm average size. Soft aggregates are disrupted by stirring in solvent dispersions. No evidence of a mesoporous structure is present. The total surface area, experimentally determined by nitrogen

adsorption/desorption isotherms (B.E.T. method), was 160–165 m<sup>2</sup> g<sup>-1</sup>. The water content, determined by TGA considering the weight loss in the 100–130 °C range, was 3–4%. The dispersive and specific components of the surface energy, measured in a previous work [27] by inverse gas chromatography (IGC), are  $\gamma_s^d = 96.0 \text{ mJ m}^{-2}$  and  $\gamma_{sp} = 142.6 \text{ mJ m}^{-2}$ , respectively.

### 2.2. Kraft lignin

LG alkali low sulfur content was purchased from Sigma-Aldrich (Milan, Italy). The declared average molecular weight was 10,000 Da and the total sulfur content determined by elemental analysis is 2.89% (w/w). The product is soluble in water giving an alkaline solution. The amount of inorganic sulfate ion was determined to be 1.3% (w/w). The ash content at 600 °C was 17% with respect to dry LG. The amount of sulfate in ash was 44% (w/w). A titration with hydrochloric acid (37% w/w, Carlo Erba Reagents, Milan, Italy) performed by pH-meter measurements showed an equivalent point at 0.026 mmol H<sup>+</sup> for 100 mg LG. For further information about characterization see Ref. [17].

### 2.3. Acid-washed lignin

Acid-washed LG was prepared by adding dropwise concentrated hydrochloric acid (37% w/w) to a Kraft LG solution (1 g L<sup>-1</sup>) up to pH 1. The precipitate was collected after filtration through 0.45 µm Nylon filters. The residue was washed with a small amount of deionized water (the total yield of the process is 60% w/w). The ash content of acid-washed LG was 0.9% (w/w) with respect to the dry compound. The sulfate content of acid-washed LG was 30 µg g<sup>-1</sup> (0.003% w/w).

### 2.4. Pyrolysis experiments

For the preparation of carbon-derivatized silica, 50 mg of LG (Kraft or acid-washed) was dissolved in a proper solvent. In the case of Kraft LG, 50 mL of deionized water was used, whereas 150 mL methanol (HPLC gradient grade, VWR, Milan, Italy) was used for acid-washed LG, due to its low solubility in water. After the complete dissolution of LG, 1 g of Zeosil silica was added, the suspension was submitted to sonication for 30 min and the solvent was removed under vacuum. For the pyrolysis, 100–200 mg of sample were placed into an alumina combustion boat. The sample was placed inside a quartz tube inserted into a cylindrical oven (Watlow ceramic fiber heater, i.d. 38 mm, length 305 mm, electrical power 600 W). The vacuum (10<sup>-3</sup> Pa) was obtained by a double stage diffusion and rotary vacuum pump. The heating rate of the oven was 600 °C h<sup>-1</sup> and the final temperature was kept for 20 min. Several pyrolysis temperatures (in the range 600–1200 °C) were explored in the above conditions. Each pyrolysis has been performed in triplicate to evaluate the reproducibility of the experiment. The reactivity of the pyrolytic carbons with atmospheric oxygen was as well investigated under ambient conditions after the pyrolysis of the material with the above reported procedure.

### 2.5. Study of the reactivity of the pyrolyzed material with nitrogen monoxide

The pyrolysis was performed by using the apparatus shown in Scheme 1 following the reported procedure with the exception that the sample (20 mg Kraft LG) was pyrolyzed directly inside an EPR quartz tube.

The sample was kept under dynamic vacuum until it reached ambient temperature, then the sample was kept under static vacuum by closing the valve on the sample. At this point, the three way valve was operated in order to connect the gas cylinder with the reservoir, that was filled with nitrogen monoxide. In order to better purify the gas, the reservoir was cooled with liquid nitrogen, then the vacuum valve was opened while keeping the nitrogen monoxide frozen. Subsequently,

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