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Preparation of mesophase pitch doped with TiO_2 or TiC particles

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Abstract

The co-pyrolysis of a petroleum residue with two different sources of titanium (tetrabutyl-ortotitanate (TBO) or titanium carbide nano-powder) was carried out to obtain mesophase pitches containing TiO_2 or TiC nanoparticles. Co-pyrolysis is an appropriate technique to achieve a good dispersion and low particle size. In the case of TBO, TiO_2 nanoparticles (5–20 nm) are observed, which are forming aggregates, the largest of them being 1–2 μm. In the case of TiC nano-particles, they are more difficult to disperse and larger aggregates are formed, although the final material is rather homogenous. The chemistry of pyrolysis for the production of doped and undoped mesophase pitches has been followed by means of solvent insolubility, XRD, XPS, FTIR and elemental analysis. They show evidences of promotion of the formation of mesophase in the presence of the titanium-containing particles, especially in the presence of TiO_2. The final materials can be of great value as precursors to produce high density titanium doped graphites for nuclear and space applications.

Keywords: Doped carbons; Mesophase; Petroleum pitch; Pyrolysis

1. Introduction

Carbon materials are good candidates for new applications in extreme environments. Some of these applications require the improvement of properties such as thermal conductivity, oxidation resistance, mechanical properties, etc. For instance, carbons materials can be used as plasma-facing components for fusion devices due to their high thermal shock resistance, absence of melting and low radiation of carbon atoms from the central plasma. In addition to these properties, this application requires a high thermal conductivity and low erosion by energetic atoms of hydrogen and oxygen [1–4]. The production of self-passivating materials using graphites doped with metallic carbides is a good method to improve the latter properties. In the last decades several investigations have been performed concerning the addition of different dopants to graphitic materials on the effects on self-passivation [1,2] and chemical erosion [3,4]. Recent investigations suggest that, besides the type of doping elements, also other aspects of their microstructure such as dopant distribution, particle size and porosity play a very critical role [3]. Titanium carbide catalyses graphitization [5], and it seems to improve mechanical properties [5,6], resistance to erosion by energetic hydrogen atoms [4,7], and thermal conductivity [8]. TiO_2 can be a good precursor to obtain TiC in situ as reaction with C can take place at temperatures higher than 1200 °C.

Mesophase pitch can be used as a precursor for the production of a great number of high performance carbon products such as high density isotropic graphite, high modulus and ultra high modulus carbon fibre, carbon fibre reinforced carbons, etc. Doped carbons have been traditionally obtained by chemical vapour deposition, which is a relatively complex and costly process [1]. Alternatively, these materials have also been obtained by using mixtures of metal carbide with coke/binder or with mesophase powders, one of the main problems of the process being the low sinterability of the carbon source with the carbides. This usually leads to the presence of inhomogeneities in the material or unwanted accumulations of the ceramic component. Several papers have been published recently reporting the synthesis of some of these doped carbons via co-pyrolysis of mixtures of pitch and a heteroatom precursor [9–11]. Co-pyrolysis is an appropriate technique because it can be performed in a conventional pyrolysis reactor, following the same process used to obtain carbon mesophase, something very interesting from the operational and economic points of view.

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The effect of the presence of “inert” particles in the pyrolysis systems has been studied by some authors and the effects are rather different depending on the chemical nature of the doping materials. For instance, cokes obtained in the pyrolysis of coal tar pitch (CTP) present agglomerations of particles called “primary QI” surrounding the mesophase spheres, which disturb the mesophase internal structure [12–14]. It seems that the presence of QI particles pins mesophase structures in its vicinity, and makes the mesophase behave as a more viscous material [15], modifying the formation, growth and coalescence of mesophase [16]. Mixtures of pitches containing particulate catalysts (usually metals or metal salts) have a similar behaviour to coal-tar pitch with QI particles but the mechanism of mesophase formation is modified seems to be different. The catalyst accelerates the formation of mesogens molecule in its vicinity, leading to mesophase surrounding the catalyst entity, thus ceasing its catalytic activity as pitch molecules cannot access to the catalyst preventing the spheres from further growth. Thus, mesophase spheres remain isolated and are of similar size. As catalyst is particulate, it can be entrapped within the sphere and be identified. Activity of the catalyst is limited as a result of not being in a homogeneous system [15].

The pyrolysis of petroleum residue in the presence of solid oxides has also been studied [17–20]. Some of them hindered hydrogen transference and lowered the size of optical textures (SiO_2-Al_2O_3, MoO_3-TiO_2, Al_2O_3, Silica gel), while others such as fusible SeO_2 improve hydrogen transfer [20]. It seems that Lewis acid properties of the oxides may play an important role in the behaviour.

This work reports the synthesis of a mesophase pitch containing TiO_2 (TiO_2 will react during graphitization to form in situ TiC particles) or TiC nanoparticles via co-pyrolysis of an aromatic petroleum residue and one of two titanium sources such as tetrabutyl-ortotitanate (TBO) and titanium carbide nano-powder (TiC). Characterization of doped mesophase pitch permits the knowledge of the chemical behaviour of the titanium compound in the polyaromatic pyrolysis system. The structure and reactivity of mixtures containing the different titanium sources are studied as a function of the titanium concentration and soaking time. These doped mesophase pitches will be used in a later work to prepare self-sintering Ti-doped graphites for use in nuclear and space applications.

2. Experimental

2.1. Pyrolysis

An aromatic petroleum residue (ethylene tar-R1) [21,22] was mixed, individually, with two different titanium sources, tetrabutyl-ortotitanate (TBO) or titanium carbide nano-powder (TiC, average particle size 100–130 nm), in an ultrasonic bath for an hour, to give mixtures of different titanium content (none, 1, 2, and 4 wt.% Ti). TBO is a liquid apparently soluble in the petroleum residue, and it decomposes during pyrolysis to give, in a multistep reaction, solid TiO_2 and pyrogenic products such as olefins, alcohols, aldehydes, ethers, etc. [23,24]. The decomposition temperature for TBO in inert organic solvents is reported to be over 300 °C, giving anatase-type and/or rutile-type nano-particles [24].

Pyrolysis of the mixtures was carried out in a laboratory-sized pilot plant previously described [21,22], using 350 g of mixture in the reactor. Pyrolysis was performed at 440 °C, soak time from 2 to 3 h and 1 MPa pressure, nitrogen being used to establish 1 MPa pressure in the system. Heating rates were constant at $\sim$20 $^\circ$C min^{-1}. The volatile material, distilled from the feedstock sample (the reactor tube is not sealed) during the heating-up stage and soak time (cracking products), was separated into gases (principally hydrogen and hydrocarbons with 1–5 carbon atoms), and liquids (naphthas and linear paraffins principally) by means of a couple of condensers. Pressure was kept constant during all the experiment (1.0 MPa) with the aid of a regulation valve. Release of pressure, from 1.0 to 0.1 MPa is carried out at the end of the pyrolysis experiment, at reaction temperature (440 °C), causing a second distillation.

2.2. Pyrolysis yield

Al the end of the experiment the mass of mesophase pitch (solid) was determined as well as the mass of liquids obtained in the condensers. The flow of gases was measured and its mass was calculated using an average molecular weight obtained by gas chromatography. Gas, liquids and solid yields are expressed in terms of the feedstock (petroleum residue + titanium compound) or in terms of the petroleum residue.

2.3. Analysis of the pyrolysis solid

The titanium content of the solid products was determined by ashing 1 g samples in air at 900 °C for 12 h. Ti content (wt.%) is determined considering that it is completely transformed into TiO_2.

To determine the mesophase content, the mesophase pitches were mounted in a resin block and the optically polished surfaces were examined by reflected polarised light. Percentage content of anisotropic phases (mesophase spheres and domains) was measured by analysing 25 fields of the solids, a total of 2500 points being counted.

Aromaticity of the solids was analysed by FTIR using a Matson Infinity Gold FTIR equipped with a MCT detector and a diffuse reflectance cell. Spectra was obtained by co-adding 100 interferograms in the range 4000–600 cm^{-1} at a resolution of 4 cm^{-1} and converted to Kubelka Munk. The spectra were baseline corrected by subtracting the nonspecific background. The areas of absorption corresponding to C-Har vibrations (2990–3150 cm^{-1}) and C-Hal (2800–2990 cm^{-1}) were obtained using the spectrometer software. The aromaticity parameter was calculated as the ratio of the two areas (C-Har/C-Hal).

The softening point of mesophase pitches was determined using a Thermomechanical Analyzer TA 2940. 0.15 gram samples of the ground semicoke (particle size < 60 μm) were heat treated under 150 ml/min nitrogen flow at 5 °C/min, using an expansion probe and a force of 0.05 N.