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Preparation of high metal content nanoporous carbon

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ABSTRACT

Activated carbons with high metal content have been prepared by the pyrolysis of ethylene tar with dissolved metal acetylacetonates (Ti, V, Fe, Co, Ni and Cu) and subsequent activation with KOH of the pitch obtained in pyrolysis. These metal compounds decompose during the pyrolysis of ethylene tar yielding metal nanoparticles formed by metal and/or oxide which are homogeneously distributed in the pitch and remain in the activated carbon, so that the concentration of metal is, in most cases, 4–5 times higher than in the pristine ethylene tar. Since KOH is an effective activating agent, all activated carbons combine a high porosity development with a high metal content. In some of the carbons, such as P2FeA (3.3% Fe, pore volume 1.84 cm^3/g, BET surface area 3270 m^2/g), there is even an increase in the pore volume when compared to the activated carbon prepared in the same way without metal, in spite of the fact that the metal increases the weight of carbon without contributing to the adsorptive capacity. It seems that iron, on the one hand modifies the pyrolysis to give a pitch with larger mesophase content and on the other hand it locally catalyzes carbon gasification with the CO_2 produced along the synthesis of the carbon. In addition to its influence on activation, iron promotes the formation of graphitic carbon fibers.

1. Introduction

High surface area activated carbons containing metals have interest in applications that require an improvement in thermal conductivity, such as storage of natural gas and hydrogen [1–6], or in their electrical properties, such as electrodes for supercapacitors [7,8], or in areas such as catalysis [9]. These materials are commonly prepared by depositing on a carbon, for example an activated carbon, a soluble metal compound which can be easily transformed into the metal. However, the amount of deposited metal is rather limited if a high surface area in the carbon is required, as metal particles may block part of the porosity [10]. Therefore, it is worthwhile to explore alternative methods to deposition. The methods based on the activation of carbon-rich precursors containing metal compounds could be particularly interesting if the metal compound can be dissolved in the carbon precursor, since a homogeneous distribution and a higher dispersion in the activated carbon are expected [5]. In this work, several metal compounds will be dissolved in a petroleum residue, ethylene tar, which will be pyrolyzed to obtain mesophase pitches that will be later activated with KOH.

KOH activation is a well-known method to prepare activated carbons with high porosity development and numerous publications can be found in the literature explaining the factors that influence porosity and pore size distribution [11,12]. Nevertheless, to our knowledge, no publications can be found where activation with KOH of carbons containing metal compounds is studied. Although it is possible that some metals react with KOH during the activation at a temperature of 700–800 °C to give soluble compounds, which are leached from the carbon during the washing-up stage, a previous work has shown that when a pitch containing metals/semimetals is activated with KOH, most of the metal/semimetal of the pitch remains on the surface of activated carbon [5].

In this work, mesophase pitches containing Ti, V, Fe, Co, Ni and Cu have been activated with KOH to obtain activated carbons with high porosity and high metal content. The influence of the kind of metal and its content in the development of porosity and in the mechanism of KOH activation of the pitches containing metals constitute the main goal of this work.

2. Experimental

2.1. Preparation

Mesophase pitches containing transition metals have been prepared by co-pyrolysis of a petroleum residue, ethylene tar, and acetylacetonates of Ti, V, Fe, Co, Ni, or Cu at 440 °C for 4 h and a pressure of 10 bars. The properties of the petroleum residue and the details of the experimental pyrolysis conditions have been described in a previous work [13–16]. The concentration of metal in the ethylene tar, expressed as percentage of metal, is 1–10 wt.%. Pitches have been labeled with the letter P followed by a number, indicating the

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starting metal concentration in the petroleum residue, and the symbol of the metal, e.g. P2Fe. As a reference, a mesophase pitch without metal has been prepared, P, in the same experimental conditions.

A mixture KOH/pitch in a 3:1 ratio was first milled in a ball mill and afterwards it was heat treated at 800 °C (in some cases at 750 °C and 700 °C) for 2 h in a N_2 flow of 100 ml/min and then it was washed to remove potassium salts. All carbons were washed identically, with distilled water in a Soxhlet for 24 h. Activated carbons are labeled by adding the letter A to the name of the starting pitch, for example P2FeA.

2.2. Properties of the activated carbons

The metal content of the activated carbon was obtained using a thermobalance TA Instruments SDT-2960 by estimation from the ashes resulting when burning the activated carbon in air flow at 1000 °C. The distribution of metal in the carbonaceous matrix has been studied by SEM (Hitachi S-3000N) and TEM (JEOL 2010 TEM). The presence of the metal/metal oxide and the degree of ordering of the pitch have been determined by X-ray diffraction (X-Ray Seifert system).

N_2 adsorption isotherms at −196 °C and CO_2 at 0 °C were obtained using a home-made fully automatized volumetric equipment designed and constructed by the Advanced Materials Laboratory (LMA), now commercialized as N_2Gsorb-6 (Gas to materials technologies www.g2mtech.com). By applying the Dubinin Radushkevich method to N_2 and CO_2 isotherms, micropore volume (V_{N2}) and the volume of micropore lower than 0.7 nm (V_{CO2}) [17], were calculated. The total pore volume (V_T) was also estimated as the amount of N_2 adsorbed by the activated carbon at 0.95 relative pressure.

2.3. Temperature-programmed reaction KOH/pitch

100 mg of a mixture KOH/pitch in a 3:1 ratio has been heat treated at 5 °C/min in helium flow of 50 ml/min to 900 °C. The amount of H_2, CO and CO_2 evolved was quantified using a mass spectrometer Omnistar Balzers. For comparison, P and P2Fe pitches without KOH, where only pyrolysis occurs, have also been studied.

3. Results and discussion

3.1. Properties of the mesophase pitches

All metal acetylacetonates used in this work decompose to metal oxide in a temperature range of 100–400 °C [18,19], and are expected to remain in the pitch after the pyrolysis. It is estimated that the metal content in the mesophase pitch is about 2.5 times larger than that initially placed in the ethylene tar, since 60% of the weight of the pristine petroleum residue is lost during pyrolysis as volatile matter.

The images obtained by SEM, Fig. 1, show metal containing particles homogeneously distributed in the pitch. TEM images of Fig. 2 indicate that the size and morphology of the particles depend on the type of metal. Thus, in P2Ni sample, particles with a size lower than 50 nm and irregular shape are observed. In P2Fe pitch the particles are larger, 100–200 nm, with regular crystal forms, whereas in P2Cu pitch discrete particles, smaller than 20 nm, alternated with larger particles with regular crystal forms are observed. It is common that particles aggregate up to 2 μm.

X-ray diffraction (XRD) spectra indicate that all copper in P2Cu pitch is as metallic copper while in pitches containing Fe or Ni, metal oxide can be found in addition to free metal. Although the pyrolysis temperature is only 440 °C, it is likely that both hydrogen and cracked hydrocarbons released during pyrolysis, in addition to the small particle size, promote the oxide reduction.

3.2. Properties of the activated carbons

Table 1 shows the values of the ash content of activated carbons. It also includes metal content, which has been estimated assuming that in the conditions selected for the determination of ash content in the carbon the most likely oxides obtained are K_2O, Fe_2O_3, CuO, NiO, TiO_2, VO_2 and CoO [20]. The ash content of the activated carbon PA is low compared with that of the other activated carbons, indicating that the washing up stage has been carried out effectively, eliminating most of the potassium compounds of the carbon. However, water has apparently not leached metal particles since in some cases the ash content exceeds 40 wt.% in the activated carbon. If there were no metal loss during the preparation of the activated carbon, it is estimated that the metal content of the activated carbon should be 5–6 times the initial content in the petroleum residue. From Table 1 it can be deduced that the ratio between the values of metal content in the activated carbon and in the petroleum residue (included in the nomenclature) is, in most cases, 4–5. In carbons such as P2FeA and P2NiA this ratio is lower. It seems that a fraction of the loaded metal is leached from the carbon during the washing-up stage.

SEM and TEM images included in Fig. 3 indicate that metal particles are well distributed in the activated carbon, presenting a size similar to that found in the pitches, indicating that there has been no substantial sintering or coalescence during the activation stage, metal aggregate sizes being lower than 3 μm. But the most remarkable fact to highlight is the formation of carbon nanofibers over the surface of the metal particles in the activated carbons containing Fe, Co or Ni (Fig. 3A). The formation of this more ordered carbon is indicative of the presence of metal particles in activated carbon.

Fig. 4 shows, as an example, the XRD spectra of two activated carbons containing iron, the activated carbon without metal (PA) and its precursor, the pitch P, as reference. The spectra of other activated carbons are included in the supporting information. The diffraction spectrum of the pitch P is typical of turbostratic carbons, exhibiting two

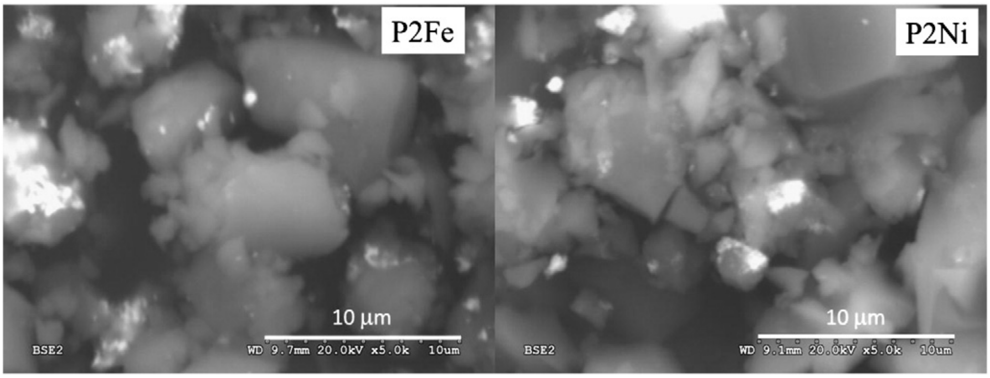

Fig. 1. Backscattered electron SEM images of the pitches: P2Fe and P2Ni.