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Effect of the stabilisation time of pitch fibres on the molecular sieve properties of carbon fibres

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Abstract

The stabilisation of pitch fibres (PFs) is the most important step for their subsequent use in the preparation of carbon fibres (CFs) and their resulting characteristics. The present work studies the influence that the stabilisation time has on the porosity of the CFs, and on the subsequent properties as carbon molecular sieve (CMS). The increase of the stabilisation time carried out at 573 K, from 2 to 8 h favours their CMS properties producing a decrease in the microposity accessible to N_2, which gets completely blocked after 6 and 8 h, while the narrow microporosity (V-DR CO_2) remains accessible. Adsorption kinetic studies with CH_4 and CO_2 were performed to assess the possibility of using these CFs as CMS by comparing them with Takeda 3A CMS. The results suggest that there is an optimal stabilisation time which allows the preparation of CFs from an abundant raw precursor with properties similar to Takeda 3A CMS.

Keywords: Pitch; Stabilisation; Fibres; Carbon molecular sieve

1. Introduction

One of the most important steps in the preparation of carbon fibres (CFs) from pitches is the stabilisation of the pitch fibres (PFs) [1]. The stabilisation of PFs consists on the oxidation of the PF molecules in order to confer infusibility to the PFs before their carbonisation. Usually, stabilisation is performed in air [1,2]. Therefore, once the PFs are stabilised they will not melt during the subsequent carbonization process and, consequently, will not lose their fibre morphology. The obtained CFs have some porosity [3] which confers them molecular sieve properties [4]. However, it is not known if the porosity of the final CFs is importantly affected by the stabilisation process time at a fixed temperature, and if this parameter (time of stabilisation) is important in the molecular sieve properties of the CFs.

Carbon molecular sieves (CMSs), are microporous carbon materials whose special textural characteristics enable kinetic separation of gas mixtures, i.e., separation as a result of differences in the diffusion rates of the species involved. CMSs can be prepared from a wide variety of carbonaceous precursors, such as lignocellulosic materials [5], coals [6,7], carbon fibres [4,8,9] and pitches [10,11] by different methods [4–14]: (i) pyrolysis of polymers, (ii) controlled gasification of chars to increase the pore size, (iii) thermal treatment of carbon precursor to modify the pore size, (iv) chemical vapor deposition (CVD) of carbon at the entrance of the pores and, (v) modification of coals by mixing with tars and resins and subsequent carbonization. In most of these cases, several steps are required in their preparation method. As an example, the CMS preparation starting from coals involves different steps: demineralisation (by acid washing), activation (with the purpose of obtaining a high pore volume), moulding, carbonisation and, finally, chemical vapour deposition (CVD) of carbon to control the pore size. The step of moulding is carried out in order to confer a geometrical external form that

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may reduce the hydrodynamic problems during their use for high flows of gases. Therefore, in general, CMS are presented in the form of pellets or monoliths.

As it has been previously commented, CFs show molecular sieve properties [4]. Their geometrical external shape presents interesting advantages compared to conventional CMS, such as: (i) low resistance to mass transfer at the surface and in the bulk due to their small diameter, (ii) a fast adsorption kinetic, (iii) very low hydrodynamic resistance, which is specially useful when these materials are to be applied in filters for high flows of gases, (iv) the fibres can be used in many different shapes (felts, cloths, etc.), (v) good mechanical properties, (vi) and finally, their use avoids the problems due to channeling and settling that exists in granular CMSs.

Taking into account all the previous comments, it seems quite interesting the development CF with appropriate molecular sieve properties. This study analyses the influence of the stabilisation time at 573 K in air in the preparation of CFs having molecular sieve properties, similar to those of commercial CMS, by a simple and novel preparation process.

2. Experimental

The CFs were prepared from an isotropic petroleum pitch. The raw pitch was characterised by Elemental analysis (CHNS Carlo Erba), solvent extraction tests (conducted with quinoline (QI) and toluene (TI) by applying the standards ASTM D 2318 and ASTM D 4072), DRIFTS (FTIR; ATI-Mattson Infinity Series) and Thermogravimetry (TG-DTA; Stanton Redcroft STA-780 Series). The softening point (SP) was measured by Thermomechanical Analysis (TMA 2940 TA Instruments) by using the expansion method. The chemical characterisation of the parent pitch is presented in Table 1.

The PFs were prepared by melt spinning in a monofilament spinning system. Details of the spinning process are available in the literature [15]. The stabilisation of the PFs was performed by placing 1 g of PFs in an alumina crucible into a horizontal furnace and heating the PFs with variable heating rates and using an air flow of 500 ml/min. The stabilisation treatment was carried out up to 573 K, and the soaking times at 573 K varied from 2 to 8 h (a conventional stabilisation process only uses 2 h of soaking time at 573 K [15]). In order to gain insight into the processes occurring during the stabilisation of the pitch fibres, DRIFT spectroscopy was used to analyse the structural characteristics of the fibres after the oxidation. Thermogravimetry (TG) was utilised to follow the weight variations during the stabilisation process.

Table 1
Characterisation of the parent pitch

Precursor	Elemental analysis (wt.%)					Solvent fractionation		
	C	H	N	S + O[a]	H/Cat[b]	IT	IQ	SP (K)
Petroleum pitch	93.73	6.16	0.09	0.01	0.79	0	0	493

[a] Oxygen and sulphur content measured by difference.

[b] Atomic ratio of hydrogen and carbon content.

The carbonisation of the stabilised PFs was performed in the same horizontal furnace at three different temperatures: 773, 1023 and 1273 K, in an inert atmosphere of N_2 and by using a gas flow of 100 ml/min. Additionally, the carbonisation of the 8 h stabilised PFs was analysed by TG under similar conditions than those used with the horizontal furnace during the carbonisation process.

The porous texture characterisation of the stabilised and carbonised PF was carried out by physical adsorption of gases (N_2 at 77 K and CO_2 at 273 K) (Quantachrome. Autosorb 6 and 6B). The samples were outgassed at 523 K under a vacuum of 1 Pa for at least 4 h. The Dubinin Radushkevich (DR) equation [16] was used to calculate the micropore volume (VDR N_2 and VDR CO_2).

Adsorption kinetic studies with CH_4 and CO_2 were carried out to assess the molecular sieve properties of the obtained CF as CMS, these CF were compared to commercially available Takeda 3A CMS. Adsorption kinetics of CH_4 and CO_2 have been followed in a constant volume DMT high pressure microbalance (Sartorius 4406) at 298 K and 0.1 MPa. The experimental results have been corrected for buoyancy effects related to the displacement of gas by sample, sample holder, adsorbed phase and pan [17].

3. Results and discussion

3.1. Study of stabilisation of pitch fibres in air

Thermogravimetry (TG) and DRIFTS were used to follow the variations produced in the fibres during the stabilisation process. Fig. 1 shows the corresponding TG profile of PFs at 573 K during 8 h.

The TG of Fig. 1 shows the variable heating rates used during the stabilisation process followed: 5 K/min up to 403 K, 1 K/min up to 493 K (soaking time of 60 min) and 1 K/min up to 573 K (soaking time of 480 min). It can be seen that the weight gain produced on the PFs as the temperature increases, which is related with the oxygen that is oxidised the pitch molecules [18–22]. This weight gain reaches a maximum of 7 wt.% at 573 K, when this temperature is kept constant, a decrease of the weight takes place. This weight loss (balance of oxygen uptake and carbon oxidation consumption) indicates that the material is being gasified by oxygen as well as suffering decomposition of the pitch molecules. In this sense, it must be remarked that DRIFT-TG studies [18] of this stabilisation process shows (even at low temperatures) oxidation of pitch molecules, intermolecular bond formation and evolution of H_2O, CO and CO_2. Even though all these processes may be occurring, the weight loss between 2 and 8 h only amounts about 3 wt.%.