



Tailoring micro-mesoporosity in activated carbon fibers to enhance SO₂ catalytic oxidation



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ARTICLE INFO

Article history:

Received 29 January 2014

Accepted 13 April 2014

Available online 24 April 2014

Keywords:

Carbon fiber
Cobalt naphthenate
Mesopores
Micropores
SO₂ adsorption

ABSTRACT

Enhanced SO₂ adsorption of activated carbon fibers is obtained by tailoring a specific micro-mesoporous structure in the fibers. This architecture is obtained via metal catalytic activation of the fibers with a novel precursor, cobalt naphthenate, which contrary to other precursors, also enhances spinnability and carbon fiber yield. In the SO₂ oxidation, it is demonstrated that the combination of micropores and large mesopores is the main factor for an enhanced catalytic activity which is superior to that observed in other similar microporous activated carbon fibers. This provides an alternative way for the development of a new generation of catalytic material.

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1. Introduction

High amounts of SO₂ are nowadays released into the atmosphere, mainly from coal-fired power plants, petroleum refineries and on-road vehicles. The atmospheric oxidation of this SO₂, which preferentially occurs in liquid phase (clouds, fog) leads to the formation of acid rain that causes health problems, acidity of soil and mineral waters and the abrasion of buildings and monuments [1–3].

In order to reduce emissions, a number of different technologies have been developed, these being mainly applied to the elimination of SO₂ in the flue gases during combustion or post-combustion stages. Most of the industrial methods used for the desulphurization of the flue gas involve a chemisorption process on alkaline sorbents such as CaO, CaCO₃ or Na₂CO₃ [4]. However, the resultant product is non-regenerable (calcium sulfite and sulfate) and they have a low commercial value. A promising alternative to these alkaline sorbents is the use of carbon materials (activated carbons or activated carbon fibers) [5] which contribute with their adsorption capacity and also act as catalysts for the oxidation of SO₂ in the presence of O₂ and H₂O (which are also typically present in flue gases). In this process, adsorbed SO₂ is oxidized into SO₃, which by hydration gives rise to diluted H₂SO₄ solutions resulting in the regeneration of the carbon material.

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Activated carbon fibers (ACF) are among the most interesting carbon materials to be used since they overcome the drawbacks derived from the high resistance to bulk gas and liquid flow characteristic of granular activated carbons. The most recent research on the preparation of such materials focused on the optimization of two main factors: (i) the porous texture of the activated carbon materials, which undoubtedly plays a crucial role in the overall process and (ii) the acid/base properties on the surface of the materials. With respect to the second factor, it is generally maintained that an increase in the basicity of the surface of these materials enhances the SO₂ adsorption capacity and the catalytic activity of the activated carbons (AC) [6–10], although their porous texture is also modified [11]. As an example, Raymundo-Piñero et al. [6] demonstrated that an enrichment in nitrogen of the activated carbon fibers enhanced their catalytic activity from values of ≈ 30 to $87 \mu\text{mol g}^{-1} \text{min}^{-1}$.

To our knowledge, the influence of the porosity on the catalytic activity has still not been satisfactorily clarified. Some authors have associated the catalytic activity of AC toward SO₂ oxidation to the presence of narrow micropores (<7 Å) [12]. On the other hand, other authors have concluded that the presence of narrow micropores binds H₂SO₄ more strongly to the surface, making its removal almost impossible by washing [13]. As far authors are concerned, the possible influence of the mesoporosity on the adsorption and desorption kinetics of activated materials in liquid phase needs to be clarified.

This work is devoted to the preparation of activated carbon fibers (ACF) with a tailored porous texture and similar surface properties (similar basicity) for their use as active catalysts for SO_2 oxidation. Melt spun coal-based carbon fibers [14–16] were activated by using two different activation processes (chemical activation with KOH and physical activation with steam). We report for the first time on the preparation of microporous–mesoporous ACF using cobalt naphthenate as a catalyst precursor to develop mesoporosity and study its influence during spinning of the mixture to produce the fibers. The two ACFs displayed a good catalytic behavior for the oxidation of SO_2 in water and the influence of micropores–mesopores architecture in the catalytic activity was determined.

2. Experimental section

2.1. Synthesis of the porous fibers

The fiber precursor used in this work (AOP) was an isotropic anthracene oil-based pitch supplied by NalonChem S.A. (Spain) with a softening point of 218°C (Mettler, ASTM D3104). 50 g of pitch was heated to 260°C at a heating rate of 5°C min^{-1} under a nitrogen flow of $20\text{ dm}^3\text{ h}^{-1}$ in a vertical stirred reactor. Cobalt naphthenate (Sigma–Aldrich, 6.5 wt.% of Co) was slowly added to the molten pitch so that the resultant doped pitch (Co-AOP) had a composition of 1 wt.% Co. The mixture was stirred at 260°C for 1 h. The Co-doped pitch, was melt-spun into fibers using a laboratory-scale device described in detail elsewhere [14]. 30 g of pitch was heated up to 242°C and extruded through a stainless steel monohole spinneret ($D = 500\ \mu\text{m}$) by applying a nitrogen pressure of 1 bar. The pitch filaments were collected on a spool operating at a winding speed of 250 cm s^{-1} . For comparison purposes, carbon fibers were also obtained from the non-doped pitch by melt-spinning at 255°C . The as-spun fibers were stabilized at 270°C under an air flow of 20 L h^{-1} at a heating rate of 1°C min^{-1} . After stabilization, the fibers were carbonized at 870°C at a heating rate of $15^\circ\text{C min}^{-1}$ with a soaking time of 15 min under a nitrogen flow of 40 L h^{-1} . The Co-doped fibers were placed in a quartz crucible, which was suspended from a thermobalance and activated with steam at 850°C until 50% burn-off was reached. Non-doped fibers were chemically activated in a horizontal furnace at 700°C for 1 h after being impregnated with KOH (KOH/Carbon fiber (wt./wt.) = 7/1). Both activated samples were washed with diluted HCl in order to remove cobalt nanoparticles from the Co-doped fibers and to remove the chemical agent and reaction products from the undoped fibers. The total absence of cobalt in Co-ACF was confirmed by ICP (Agilent 7700x).

Characterization of the ACF: The elemental analysis of AOP, ACF and Co-ACF was performed by using a LECO-CHNS-932 micro-analyzer and a LECO-VTF-900 furnace coupled to a microanalyzer. X-ray photoelectron spectroscopy (XPS) was carried out in a Specs spectrometer using Mg $K\alpha$ (1253.6 eV). The C1s and O1s high resolution spectra were curve-fitted using a Gaussian–Lorentzian peak shape (see Supporting Information for details). The pH of ACF and Co-ACF was measured according to the ASTM D 3838-80 standard. The textural parameters of ACF and Co-ACF were determined from the N_2 adsorption–desorption isotherms at 77 K (Nova 2200, Quantachrome). The samples were previously outgassed overnight at 300°C . The specific surface area (S_{BET}) was calculated using the BET method. The amount of nitrogen adsorbed at a relative pressure of $p/p_0 = 0.96$ was used to determine the total pore volume (V_{T}). The micropore volume (V_{micro}) was estimated from the Dubinin–Radushkevich equation. The BJH method was applied to the desorption branch of the N_2 isotherms to calculate the mesopore volume (V_{meso}). Pore size

distributions (QSDFT and BJH) were also calculated from the isotherm data. The morphology and cobalt distribution in the fibers after activation were monitored on a scanning electron microscope (SEM) using an Evo LS15 Zeiss microscope coupled to an energy-dispersive X-ray spectrometer (EDX) Bruker 29 eV and a back-scatter detector (BSE) for elemental characterization.

2.2. Catalytic activity

The catalytic activity toward SO_2 oxidation was studied by following a procedure described elsewhere [17]. A saturated solution of SO_2 was prepared by bubbling pure SO_2 through distilled water for several minutes. The saturated solution was diluted until the concentration of SO_2 reached a value of $1.65 \times 10^{-3}\text{ M}$. The concentrations of the saturated and diluted solutions were determined by titration with iodine using starch as indicator. 250 mL of diluted solution was saturated in oxygen by blowing air for several minutes. The air bubbling was kept up through the whole experiment. The reaction temperature was set at 25°C by using a thermostatic bath. Once the temperature and the conductivity were stable (25°C , $\sim 570\ \mu\text{S cm}^{-1}$), 0.3 g of sample was added to the stirred solution. The oxidation reaction was followed by conductometry, by means of a high precision (Mettler Toledo) conductometer. Due to the hydrophobicity of the samples, 3 mL of distilled water was used to wet the samples for several minutes prior to their introduction into the reactor. Blank measurements in the absence of fibers were also conducted.

3. Results and discussions

3.1. Activated carbon fibers with tailored porous textures

Two activated carbon fibers with controlled porous texture were prepared, a microporous activated carbon fiber (ACF) and a microporous–mesoporous activated carbon fiber (Co-ACF), obtained from a coal-based carbon fiber (CF) and a Co-doped carbon fiber (Co-CF), respectively.

ACF was produced by chemical activation with KOH of a carbon fiber (diameter of $27\ \mu\text{m}$, Fig. 1a) obtained by melt spinning, stabilization and carbonization of an anthracene oil-based pitch (AOP, softening point of 218°C), a coal derivative obtained by pyrolysis of anthracene oil [14,15]. The KOH/fiber ratio used in the activation was 7/1.

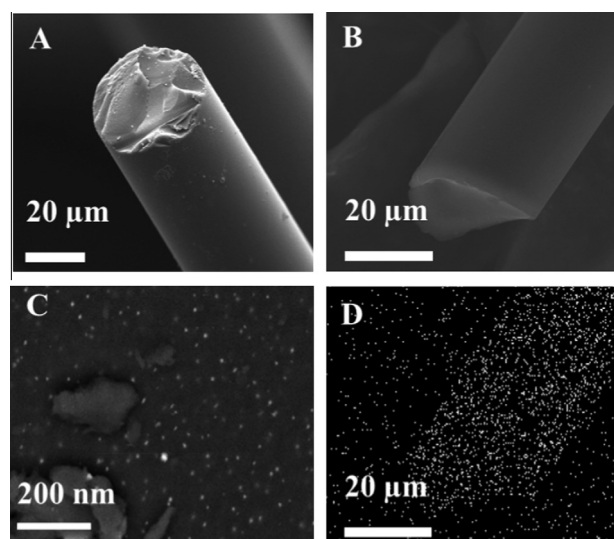


Fig. 1. (A) SEM images corresponding to the ACF precursor. (B) SEM, (C) BSE and (D) EDX-Co mapping of B, corresponding to the Co-ACF precursor.

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