

Developing microporosity in Kevlar[®]-derived carbon fibers by CO₂ activation for CO₂ adsorption



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ABSTRACT

A series of activated carbon fibers (CFs) has been prepared from Kevlar[®] by carbonization and subsequent CO₂ activation. The resulting materials exhibited the specific surface areas in the range of 50–1240 m²/g, total pore volumes in the range of 0.02–0.61 cm³/g, and micropore volumes in the range of 0.02–0.54 cm³/g. The well-developed microporous structure resulted in very good CO₂ adsorption properties; the best uptake was 6.58 mmol/g of CO₂ (at 0 °C and p = 800 mmHg). The CO₂ activated Kevlar[®]-derived CFs achieved better CO₂ uptakes than analogous carbons activated in KOH, but the latter outperformed them in benzene adsorption. We concluded that almost exclusively ultramicroporous (w < 1 nm) CO₂-activated CFs adsorbed more CO₂ due to the presence of small micropores, whereas the KOH-activated carbons possessed larger micropores, which are essential for adsorption of benzene and related molecules. An additional advantage of the CO₂ activated Kevlar[®]-derived CFs is the preservation of fiber morphology, which can be destroyed during KOH activation.

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1. Introduction

Activated carbon fibers (ACFs) continue to gain a lot of attention due to their interesting properties and diverse applications [1]. These materials often have high specific surface area, large pore volume, and high fraction of micropores and ultramicropores (w < 0.7–1.0 nm). These features result in exceptionally good sorption properties: especially high uptakes and fast kinetics (both in gas and liquid phases) [2–10].

Because of the well-developed structure and high versatility of ACFs, these materials have been employed in various applications, mostly in water and air treatments [11,12]. Some examples include the removal of copper and nickel from contaminated water [13], removal of HCl (ACFs after modification with ammonia) [14], adsorption of SO_x and NO_x [2,3,15], removal of volatile organic compounds from air [4–6], and other organics from water [7]. In addition, ACFs have been used in adsorption of methane [16,17], CO₂ [18–20], and CS₂ [21]. Furthermore, silver-containing ACFs have shown antibacterial properties against *Escherichia coli* and

Staphylococcus aureus [22,23]. These few examples show the versatility and potential of ACFs.

ACFs are usually prepared from polymeric precursors that already have fiber morphology, such as: polyacrylonitrile (PAN) [24,25], polyacrylonitrile and polyvinyl acetate [1], viscose [22], aramid Nomex [poly(*m*-phenylene isophthalamide)] [5,18], pitch-based materials [2,13], phenolic resin [19,26], petroleum pitch and melamine resin [27], polyvinyl chloride (PVC) [28], polyvinyl alcohol (PVA) [29], polyaniline (PANI) [30], Kevlar[®] (poly(*p*-phenylene terephthalamide)) [31–34], cellulose [11,35], and many more. For instance, Martinez-Alonso et al. [31] prepared ACFs from Kevlar[®] fibers by carbonization at 900 °C in argon atmosphere and subsequent CO₂ activation at 800 °C. One of the best ACFs had the BET specific surface area of 986 m²/g, total pore volume of 0.50 cm³/g, micropore volume of 0.43 cm³/g, and ultramicropore volume of 0.28 cm³/g. Giraldo et al. [32] prepared ACFs from Kevlar[®] as well, but carbonized the fibers at 800, 900, and 1000 °C in flowing nitrogen and subsequently, activated them at 750 °C for 1 or 2 h using water vapor. The best material had specific surface area of 460 m²/g and micropore volume of 0.24 cm³/g.

In this work, we report the preparation of activated carbon fibers from Kevlar[®] fibers with better structural properties for CO₂ adsorption than the previously reported samples. This study shows

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that the activation of the carbonized Kevlar[®] fibers in CO₂ preserves fiber morphology and enhances ultramicroporosity, which is essential for CO₂ adsorption at ambient conditions, while this is not the case for activation of this fiber material in KOH [36].

2. Experimental

2.1. Materials

The activated carbon fibers were prepared from Kevlar[®] fibers using the following procedure: first, 5 g of Kevlar[®] (DuPont Warsaw, Poland) was dried at 100 °C for 3 h in an oven. Next, the fibers were carbonized at 550 °C for 30 min using 10 °C/min temperature ramp in nitrogen flow (0.9 dm³/min; all flow rates measured at room conditions: ≈22 °C and ≈1 bar). The resulting carbon fibers were then activated with CO₂ using the following procedure: 1 g of the carbon fibers was placed in a quartz tube in an electric furnace. Then, the fibers were heated to either: 700, 750, or 800 °C using 20 °C/min temperature ramp in nitrogen flow (0.3 dm³/min). Once at the target temperature, the flow was switched to CO₂ (0.3 dm³/min) and the activation was carried for either 0.5, 1, 3, or 5 h. Afterwards, the flow was switched back to nitrogen (0.3 dm³/min) and the samples were allowed to cool down to room temperature.

The carbonized carbon fibers were labelled KEV-C, and the activated carbon fibers were labelled KEV-x-y, where *x* designates the activation temperature and *y* designates the activation time. The following samples were prepared: KEV-700-1, KEV-700-5, KEV-750-1, KEV-750-3, KEV-800-0.5, and KEV-800-1.

An activated carbon powder KEV-4-KOH from Ref. [36] was used as a reference in this work. The powder was prepared by carbonization of Kevlar[®] fibers at 700 °C for 30 min in nitrogen flow and activation with KOH using 4:1 wt ratio of KOH to carbon.

2.2. Measurements

Nitrogen adsorption–desorption isotherms were measured at –196 °C and CO₂ adsorption isotherms were measured at 0 °C using a surface area and porosity analyzer ASAP 2020 manufactured by Micromeritics Instrument Corp., Norcross, GA, USA. In addition, KEV-750-3 activated carbon fibers were tested for CO₂ adsorption at 0 °C, 10 °C, and 25 °C. The latter data were used to calculate the isosteric heat of adsorption for this material, using the Clausius–Clapeyron equation.

Benzene adsorption isotherms were measured at 20 °C using the McBain–Bakr gravimetric method with a homemade apparatus equipped with a quartz-spring balance. Each sample was degassed

at 200 °C for 2 h in vacuum. Scanning electron micrographs were taken with a scanning electron microscope (SEM) LEO 1530 manufactured by Zeiss, Germany. The acceleration voltage was 2 kV. Optical photographs were taken with a 500D photo camera manufactured by Canon, Japan.

Elemental analysis (EA) was measured using a Vario MICRO Cube apparatus (Germany). The oxygen content O% was calculated as $O\% = 100\% - C\% - H\% - N\% - S\%$.

3. Results and discussion

The goal of this work was to use Kevlar[®] fibers to prepare activated carbon fibers (ACFs). CO₂ activation was used to develop possibly large specific surface area, micropore volume, and ultramicropore volume, but with retention of the fiber morphology. The former were targeted to achieve high CO₂ and benzene uptakes.

Fig. 1 shows photographs of Kevlar[®] fibers, the KEV-C carbon fibers, KEV-750-3 activated carbon fibers, and KEV-4-KOH activated carbon powder. Noteworthy, neither carbonization nor CO₂ activation destroyed the Kevlar's[®] fiber morphology, resulting in a cloth-like activated carbons. The latter may be advantageous in some sorption and/or separation applications. In contrast, KOH activation has destroyed the Kevlar's[®] morphology, as observed in Fig. 1D [36].

Fig. 2 shows scanning electron micrographs of Kevlar[®] fibers, KEV-C carbon fibers, KEV-750-3 and KEV-800-0.5 CO₂-activated carbon fibers. Kevlar[®] fibers diameter was ≈9.9 μm, while the carbonized fibers had diameter of ≈7.6 μm, showing that, as expected, the fibers have shrunk due to carbonization. The ACFs had diameters ≈7.0 μm (KEV-750-3) and ≈7.7 μm (KEV-800-0.5). In addition, the carbon fibers and ACFs had a noticeably rough surface as compared with the Kevlar[®] fibers, presumably as the result of porosity creation.

Table 1 lists elemental composition of the Kevlar[®] fibers, KEV-C carbon fibers, and KEV-750-3 CO₂-activated carbon fibers. The Kevlar[®] fibers' composition is similar to that reported elsewhere [31]. Interestingly, KEV-C carbon fibers exhibit a similar composition to that of the original Kevlar[®] fibers (for the main elements the difference did not exceed a couple of percentages). In addition, KEV-C carbon fibers contain almost 12% of nitrogen, which is quite high for a carbon material; thus, they may be of interest for applications benefiting from nitrogen presence. The KEV-750-3 activated carbon fibers still have similar composition to the precursor fibers, differing mostly in nitrogen and oxygen. The nitrogen content was halved and the oxygen content was doubled due to activation process.

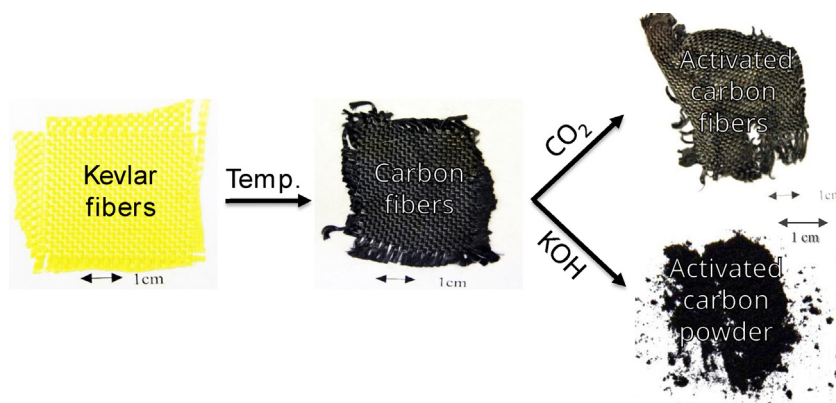


Fig. 1. Photographs of Kevlar[®] fibers, KEV-C carbon fibers, KEV-750-3 CO₂-activated carbon fibers, and KEV-4-KOH activated carbon powder.

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