



Novel synthesis of a micro-mesoporous nitrogen-doped nanostructured carbon from polyaniline



A. Silvestre-Albero^a, J. Silvestre-Albero^a, M. Martinez-Escandell^{a,*}, M. Molina-Sabio^a,
A. Kovacs^b, F. Rodriguez-Reinoso^a

^a Laboratorio de Materiales Avanzados, Departamento de Química Inorgánica – Instituto Universitario de Materiales, Universidad de Alicante, Ap. 99, E-03090 Alicante, Spain

^b BroadBit, BroadBit Slovakia s.r.o., Eötvösöva ul. 12, 945 01 Komárno, Slovakia

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ABSTRACT

Nanostructured carbons with relatively high nitrogen content (3–8%) and different micro and mesoporosity ratio were prepared by activation of polyaniline (PANI) with a ZnCl₂–NaCl mixture in the proportion of the eutectic (melting point 270 °C). It was found that the activated carbons consisted of agglomerated nanoparticles. ZnCl₂ plays a key role in the development of microporosity and promotes the binding between PANI nanoparticles during heat treatment, whereas NaCl acts as a template for the development of mesoporosity of larger size. Carbons with high micropore and mesopore volumes, above 0.6 and 0.8 cm³/g, respectively, have been obtained. Furthermore, these materials have been tested for CO₂ capture and storage at pressures up to 4 MPa. The results indicate that the nitrogen groups present in the surface do not seem to affect to the amount of CO₂ adsorbed, not detecting strong interactions between CO₂ molecules and nitrogen functional groups of the carbon, which are mainly pyridinic and pyrrolic groups.

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1. Introduction

Nanostructured carbons [1–3] have a large number of applications such as adsorbent for water purification or elimination of contaminants [4], proteins sorption [5], energy applications such as hydrogen and methane storage [6–10], components of lithium batteries and supercapacitors [11–15], or environmental applications such as CO₂ capture [16].

Nitrogen-doped carbons with high surface area have recently shown remarkable research interest to improve the reversible capacity of lithium batteries [17–19] or the specific capacity in supercapacitors [20,21]. On the other side, it has been reported that the introduction of nitrogen-containing basic groups in the carbon framework may help to improve the interaction of the carbon surface with CO₂ [22,23] and, consequently, the amount of CO₂ adsorbed.

Conventional preparation methods of nitrogen doped carbons involve: i) carbonization of nitrogen-containing precursors or

organic nitrogen-compounds [23]; ii) impregnation of porous carbons with nitrogen containing organic-compounds and subsequent heat treatment [24]; or iii) heat treatment of the porous carbon material with nitrogen-containing gases (e.g. NH₃) [22]. Recently, the preparation of nitrogen doped carbons using eutectic mixtures as template and ionic liquids as nitrogen-carbon precursor has been reported [25]. Others porous materials through the use of ionic liquids and eutectic mixtures have also been reported [26–30].

Polyaniline (PANI) has proved to be a very interesting precursor for the production of nitrogen-doped carbon nanostructures [31–33]. The preparation involves conventional physical or chemical activation. The activated carbons obtained with these two approaches usually are microporous with a substantial loss of nitrogen during activation [34–37]. This paper reports the preparation of nitrogen doped nanostructured porous carbons with high mesopore volume using a eutectic salt (ZnCl₂ + NaCl) as activating agent and polyaniline as carbon and nitrogen source. The effect of the salt content as well as the carbonization conditions is analyzed. Finally, the role of porosity and surface chemistry on the CO₂ capture ability of the carbons will be discussed.

* Corresponding author. Tel.: +34 96 590 3537; fax: +34 96 590 3454.

E-mail address: manolo.m@ua.es (M. Martinez-Escandell).

2. Experimental

2.1. Polyaniline preparation

The synthesis of PANI was carried out using a procedure similar to the one described by Li et al. [38], but using stoichiometric amounts of aniline and ammonium persulfate in 1 M H₂SO₄. Polymerization reaction was carried at 0 °C for 4 h. After the polymerization the sample was filtered and then washed with water and acetone. Finally, the polymer was dried at 60 °C under vacuum for 12 h. The H₂SO₄-doped PANI emeraldine salt was obtained.

2.2. Activated carbon preparation

PANI was carbonized under a nitrogen flow (80 mL/min) for 2 h in a tubular furnace at 550 °C and 800 °C (PANIC550 and PANIC800).

Two activated carbons were prepared by mixing 4 g of PANI with 30 g of the eutectic salt ZnCl₂/NaCl (58:42% M) freshly prepared in a ball mill for 30 min at 300 rpm. After that, the mixture was heat treated in N₂ flow (80 mL/min) at 550 °C or 800 °C for 4 h and then washed, first with a hot 10% HCl solution for 24 h in a Soxhlet apparatus to remove the salts, and then with water until the elimination of chlorides (carbons PANI_30NaZn_550 and PANI_30NaZn_800). Part of the carbon PANI_30NaZn_550 (already washed) was heat treated in nitrogen flow (80 mL/min) to 800 °C for 4 h (PANI_30NaZn_550_800).

Two other activated carbons have been prepared in the same way but using a lower content of the eutectic salt; 4 g of PANI were mixed with 2 g or 8 g of the eutectic salt, carbons PANI_2NaZn_550 PANI_8NaZn_550, respectively. For reference, two carbons have been prepared using the individual components of the eutectic mixture at 550 °C. In these carbons the mixture was 4 g of PANI and 7.2 g of NaCl (PANI_7Na_550) and 4 g of PANI and 22.8 g of ZnCl₂ (PANI_23Zn_550).

2.3. Characterization

Thermogravimetric analysis were carried out under a nitrogen flow of 100 mL/min using a heating rate of 10 °C/min up to 1000 °C in a TGA/SDTA851e/LF/1600 system from Mettler Toledo.

The morphology of the materials was analyzed employing a scanning electron microscope (SEM) HITACHI S-3000N. Transmission electron microscopy (TEM) images were obtained with a JEOL JEM-2010 microscope.

Nitrogen content of the carbons was obtained in a LECO CHNS analyzer with a Micro TruSpec detector.

The X-Ray diffraction patterns of the powder were obtained in a Siefert JSO 2002 Debye Flex system, using the Bragg–Brentano geometry and the CuK α -1 radiation operating at 40 mA and 40 KV. The scan speed used was 1° every 2 min.

Raman spectra were obtained using a Horiba Jobin-Yvon Lab-Ram Raman Confocal Microscope system. The spectrometer was operated in continuous scanning mode in the range of 500–1700 cm⁻¹ using argon-ion laser of wavelength $\lambda = 514.5$ nm.

X-ray photoelectron spectroscopy (XPS) analysis was used to obtain information of the nitrogen groups. A V.G. Scientific Microtech Multilab spectrometer with a MgK α achromatic X-ray source was used. The pressure inside the analysis chamber was held below 5 · 10⁻⁷ Pa during the course of the analysis.

Gas adsorption measurements (N₂ at -196 °C and CO₂ at 0 °C) up to atmospheric pressure were performed in a home-made fully automated equipment now commercialized as N₂Gsorb-6 [39]. Before any experiment, samples were degassed (10⁻⁴ Pa) at 250 °C

for 4 h. Surface area and micropore volume, V_{N₂}, were estimated from the nitrogen adsorption data after application of the BET and the Dubinin–Radushkevich equations, respectively. The volume of mesopores (V_{meso}) was calculated by subtracting the micropore volume (V_{N₂}) from the total pore volume, estimated as the amount adsorbed at P/P₀ ≈ 0.98. CO₂ adsorption data at 0 °C were used to determine the narrow micropore volume (V_{CO₂}), after application the DR equation. Non Linear Density Functional Theory (NLDFT) to the carbon dioxide adsorption data were used to estimate the volume of pores below 0.66 nm.

2.4. High-pressure adsorption measurements

CO₂ adsorption capacity was measured at 25 °C and up to a final pressure of 4 MPa in a home-made fully automated manometer equipment now commercialized as iSorbHP by Quantachrome Instruments. Before the adsorption experiment, samples were degassed at 300 °C for 4 h.

3. Results and discussion

3.1. Characterization of the activated carbons

Fig. 1 shows the weight variation with temperature experienced by the raw polymer. A three step decomposition of PANI takes place, which is similar to that described by other authors [40,41] being attributed to the evolution of water, loss of dopants and eventually breakdown of the polymer backbone. Some authors [42,43] have shown that, in addition, a non-reversible chemical crosslinking reaction occurs without weight loss around 200 °C, restricting the mobility of the polymer molecular chains, and avoiding the softening or the melting of the polymer.

The shape of the curve for the PANI is rather similar to that of PANI-eutectic salt up to 570 °C, although its weight loss is much lower due to the lower proportion of the polymer in the mixture. Since the eutectic melting point is 270 °C, it can be expected that, above this temperature, the liquid mixture of ZnCl₂ and NaCl infiltrates within PANI particles, affecting the crosslinking reactions of the polymer and even the subsequent decomposition. The high weight loss observed above 570 °C is mainly assigned to the evaporation of ZnCl₂, although the yield values found in Table 1 indicate that there must also be a reaction between PANI and eutectic salt, causing the formation of pores. In fact, solid yield only changes from 55 to 45 wt% when increasing PANI carbonization temperature, but changes from 43 to 20 wt% are observed when using the eutectic salt.

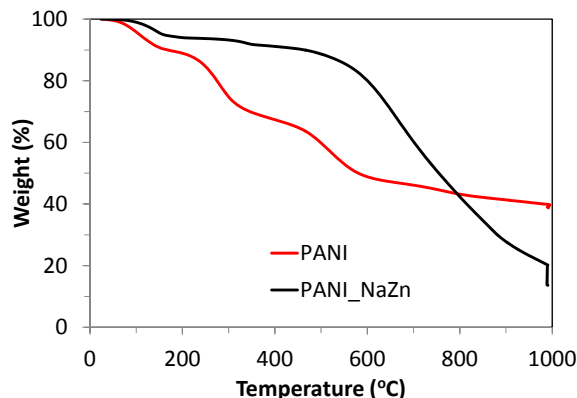


Fig. 1. TG curves of PANI and PANI-eutectic salt (ratio 4:30).

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