Carbon 115 (2017) 539–545

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Unusual flexibility of mesophase pitch-derived carbon materials: An approach to the synthesis of graphene

D. Barreda [a], A.M. Pérez-Mas [a], A. Silvestre-Albero [b], M.E. Casco [b], S. Rudić [c], C. Herdes [d, e], E.A. Müller [d], C. Blanco [a], R. Santamaria [a, **], J. Silvestre-Albero [b, *], F. Rodríguez-Reinoso [b]

[a] Instituto Nacional del Carbón (INCAR-CSIC), Apdo. 73, 33080, Oviedo, Spain
[b] Laboratorio de Materiales Avanzados, Departamento de Química Inorgánica, Universidad de Alicante, E-03690, San Vicente del Raspeig, Spain
[c] ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, OX11 0QX, UK
[d] Department of Chemical Engineering, Imperial College London, South Kensington Campus, London, SW7 2AZ, UK
[e] Department of Chemical Engineering, University of Bath, Claverton Down, Bath, Somerset, BA2 7AY, UK

ARTICLE INFO

Article history:
Received 7 October 2016
Received in revised form
30 December 2016
Accepted 15 January 2017
Available online 16 January 2017

ABSTRACT

Structural flexibility in a petroleum pitch-derived carbon material has been indirectly evaluated using X-ray diffraction (XRD), immersion calorimetry and inelastic neutron scattering (INS) measurements. Exposure of the carbon material to an organic solvent (e.g., *n*-nonane) gives rise to a large internal rearrangement, associated with a drastic re-ordering of the graphitic microdomains. These structural changes are also associated with a high flexibility of the internal porous network, as observed by inelastic neutron scattering measurements. The internal rearrangement and the structural flexibility could be responsible for the excellent performance of this kind of activated carbons in a wide variety of adsorption processes. Last but not least, the structural characteristics of these carbon materials composed of graphitic microdomains has been used to synthesize graphene "egg-like" flakes following a simple procedure based on exfoliation with organic solvents.

1. Introduction

Nanoporous materials with a well-developed porous structure and surface chemistry constitute one of the main pillars in nanotechnology. These solids include zeolites, activated carbons, ordered-mesoporous silicas (OMS), metal-organic frameworks (MOF), among others. One of the main concerns in the design and synthesis of these nanoporous materials is the knowledge of their porous structure, since the size and the shape of the pore cavities will define their performance in a given application (for instance in gas adsorption/separation processes, as a sensor, in drug delivery processes, as a catalyst, etc.). Traditionally, the porous structure of nanoporous solids has been evaluated by gas adsorption at cryogenic temperatures (e.g., N_2 at 77 K and Ar at 87 K) [1,2]. Assuming a rigid structure for the porous solid, the monolayer formation in the surface can be used to estimate the "apparent" surface of the material after application of the corresponding mathematical equations (e.g., BET equation). However, it is well known that this assumption is not always accurate for certain nanoporous solids due to the presence of adsorption-induced deformation phenomena upon an external stimuli (e.g., pressure and/or temperature changes, exposure to a certain probe molecule, etc.). Whereas this phenomenon has been widely established for MOFs (for instance the gate-opening effect in ZIF-8 or MIL-53) [3,4], it is sometimes neglected in the evaluation and understanding of other porous solids. These structural changes are due to the substantial stress that takes place in the inner cavities of the solid upon adsorption (in the order of GPa), thus giving rise to contractions, swelling and morphological transitions. For instance, Monte Carlo simulations for methane adsorption in slit-shaped carbon narrow micropores (0.315 nm in size) provided an *adsorption stress* or *solvation pressure ca.* 1.8 GPa at 19 MPa [5]. Similar studies of argon in carbon-slit nanopores suggest an enhancement of the tangential pressure of ~20 000 times the normal bulk pressure [6]. Interestingly, these phenomena are not exceptional and have been identified for a wide range of materials including activated carbons [5–10], mesoporous silicas [11], zeolites [12], etc. Despite the relevance of these adsorption-induced phenomena defining the final porous structure

---

* Corresponding author.
** Corresponding author.
E-mail addresses: riqui@incar.csic.es (R. Santamaria), joaquin.silvestre@ua.es (J. Silvestre-Albero).

http://dx.doi.org/10.1016/j.carbon.2017.01.046

under *operando* conditions and consequently, the final performance of the nanoporous system, their presence has been traditionally neglected. This is due to the difficulty in assessing these structural changes, particularly in amorphous systems such as carbon materials. However, *in-situ* dilatometry measurements performed in mesoporous silicas and carbon materials upon adsorption suggest that these structural characteristics depends on the adsorbate used, the adsorption temperature and the pore size, these changes being rather small (swelling not exceeding 1%) [9,13]. These findings have been corroborated by mathematical calculations using density functional theory (DFT) and Monte Carlo simulations.

Recent reports described in the literature point to activated carbons derived from petroleum residues as being among the highest performing materials to date for a wide range of applications ranging from high-pressure methane storage, CO_2 capture, benzene and toluene adsorption, energy storage in electric double layer capacitors, etc., surpassing conventional activated carbon materials [14–16]. This outstanding performance has been rationalized by the presence of a highly developed porous structure (narrow micropore volume above 1 cm^3/g) and a BET surface exceeding 3200 m^2/g. The crux of the matter is that these metrics obtained for a carbon derived from a graphitizable residue cannot be exclusively justified considering a perfectly rigid arrangement of graphitic crystallites. Furthermore, the large BET surface area achieved exceeds the theoretical value for a single graphene layer (2630 m^2/g), shedding a shadow on the above-mentioned results.

With this in mind, the main goal of the present work is to evaluate the presence of structural changes in petroleum-pitch derived activated carbons upon adsorption of different organic molecules (including crystallite reorientation and swelling/contraction phenomena) and to determine if it is this aspect of the material that accounts for the exceptionally high adsorption performance. As an ancillary result, the unexpectedly high flexibility in these materials will be exploited to synthesize graphene. Compared to conventional processes for graphene production, e.g., via oxidation followed by exfoliation/thermal reduction of graphite, the present proposed method, based on an exfoliation treatment with *N*-methyl-2-pyrrolidone (NMP), constitutes a simple and expedite approach.

2. Experimental section

2.1. Preparation of the carbon sample

The activated carbon evaluated in this study was prepared from a petroleum mesophase pitch (PP) obtained from a vacuum residue (VR). The mesophase pitch and the KOH (KOH:precursor ratio of 6:1 (w/w)) were initially mixed in a ball mill for 30 min, and subsequently submitted to an activation treatment in a horizontal furnace at 1073 K for 2 h, under a nitrogen flow (100 mL/min). The as-synthesized material was washed with 10% HCl solution and distilled water until complete removal of the chloride ions.

2.2. X-ray diffraction measurements

X-ray diffraction measurements of the activated carbon before and after chemical treatment with *n*-nonane and methylene blue were performed using a Bruker D8-Advanced equipment with a KRISTALLOFLEX K 760-80F X-ray generator and a copper anode ($\lambda = 1.54056$ Å). Pre-impregnation with *n*-nonane was performed using an excess of the liquid to saturate the sample, followed by an overnight outgassing treatment at 298 K to selectively remove the excess of *n*-nonane from large pores, as described elsewhere [17]. Under these conditions only narrow micropores (those below 1 nm) remain filled with *n*-nonane. Methylene blue (MB) pre-impregnation was performed in aqueous phase using the standard method reported in the Deutsches Arzneibuch.

2.3. Immersion calorimetry measurements

Immersion calorimetry measurements were performed in a Tian-Calved C-80D calorimeter at 303 K. A full description of the experimental set-up can be found elsewhere [18]. Before the immersion calorimetry measurements with benzene and alpha-pinene, activated carbon was outgassed at 523 K for 4 h.

2.4. INS measurements

Inelastic neutron scattering (INS) experiments were performed using the TOSCA spectrometer at the ISIS Neutron and Muon Pulsed Source, Rutherford Appleton Laboratory in the UK [19]. Before the experiment, 1.0 g of activated carbon was pre-adsorbed with the appropriate amount of liquid *n*-nonane to completely fill the pore cavities (total pore volume was obtained from the N_2 adsorption isotherms at 77 K). The pre-impregnated sample was wrapped in Al-foil and loaded into the high-pressure stainless steel cell supplied by ISIS. INS measurements were done at 4 K. After the first experiment with the saturated sample, the system was pumped under vacuum at 298 K for 4 h to remove *n*-nonane from large cavities [17]. To end up, the sample was pressurized with methane gas (6 MPa) at 275 K for 3 h before cooling down to 4 K using a closed cycle refrigerator (CCR).

Computational analysis of INS data was done using the mixed Monte Carlo multiple minimization and Large Scale low mode method, as implemented in the MacroModel software (Schrödinger), until no additional new structures were obtained. All conformations of *n*-nonane with relative energies $\leq$7.8 kJ/mol were subsequently submitted for geometry optimization using the Gaussian 09 suite of programs [20] and density functional theory (DFT) at the B3LYP/6-311++G(d,p) level. This led to a new set of relative energies (corrected to zero point energies), molecular structures and (harmonic) vibrational spectra, which could then be compared with experiment. More accurate energies were calculated for the optimized DFT structures, at the MP2/6-311++G(d,p) level of theory. All energies were corrected for zero point energy using the un-scaled DFT harmonic frequencies. The theoretical inelastic neutron scattering (INS) transition intensities were derived from the calculated normal mode eigenvectors, and the corresponding spectra were simulated using the aCLIMAX program [21].

2.5. Molecular simulations

Classical Molecular Dynamics simulations were performed using the coarse-grained SAFT forcefield [22,23]. An empty rigid graphitic pore of 1 nm was exposed to an excess of nonane molecules at 275 K until pore filling was achieved. The resulting system was then exposed to a reservoir of methane molecules and the pressure increased by compressing the bulk volume until a pressure of 6 MPa was achieved. More information can be found in the Supporting Information.

2.6. Preparation of graphene from PP-AC

PP-AC carbon was dispersed using two different organic solvents, *N*-methyl-2-pyrrolidinone (NMP, spectroscopic grade, Aldrich) and *N*,*N*-dimethylformamide (DMF), at a concentration of 5 mg/mL (200 mL, round-bottomed flask). The dispersion was then sonicated (Bransonic Ultrasonic 5510-MTH, 135 W-42 kHz) for 15 min.