



Diffusion of molecular hydrogen in carbon aerogel



Emanuel Bahn ^{a, b, **}, Orsolya Czakkel ^a, Balázs Nagy ^c, Krisztina László ^c,
Silvia Villar-Rodil ^d, Juan M.D. Tascón ^d, Franz Demmel ^e, Mark T.F. Telling ^{e, f},
Peter Fouquet ^{a, *}

^a Institut Laue-Langevin, CS 20156, F-38042 Grenoble Cedex 9, France

^b Cavendish Laboratory, J.J. Thompson Avenue, Cambridge CB3 0HE, UK

^c Department of Physical Chemistry and Materials, Budapest University of Technology and Economics, H-1521 Budapest, Hungary

^d Instituto Nacional del Carbón, INCAR-CSIC, Apartado 73, 33080 Oviedo, Spain

^e ISIS Facility, Rutherford Appleton Laboratory, Chilton OX11 0QX, UK

^f Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, UK

ARTICLE INFO

Article history:

Received 18 June 2015

Received in revised form

6 November 2015

Accepted 10 November 2015

Available online 17 November 2015

ABSTRACT

The diffusion of hydrogen molecules adsorbed in a highly porous carbon aerogel has been studied with quasi-elastic neutron scattering. Hydrogen diffusion in this carbon substrate followed an activated jump process with a single activation barrier. The temperature dependence of the diffusion rate agrees well with previous results from activated carbons and other highly porous carbons. The carbon aerogel sample showed a strongly enhanced conversion between the ortho- and para-hydrogen spin states. The ortho-para conversion process, however, was inhibited for a fraction of the hydrogen molecules. This inhibition process is attributed to a rotational confinement of the hydrogen molecules at the nanometre scale.

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1. Introduction

The adsorption and diffusion of molecular hydrogen in carbon materials is of fundamental interest in various fields. The potential use of porous carbons and carbon nano-structures for hydrogen storage, in particular, has motivated a large number of investigations in recent years [1–3]. Experimental studies have targeted various specific carbon systems, such as nanofibers [4], nanotubes [1,5,6], nanohorns [7], porous carbons [8], and carbon aerogels [9]. Calculations have been performed for the adsorption on carbon nanofibers, on and in nanotubes as well as in pores [10–12].

The structure of an adsorbed layer of molecular hydrogen on the basal plane of graphite has been studied by, e.g., neutron scattering [13]. For temperatures below 22 K, these experiments revealed a commensurate $\sqrt{3} \times \sqrt{3} R 30^\circ$ structure for coverages up to a full monolayer (ML) and an incommensurate dense layer at higher

coverages. Analytical calculations agreed with these experimental results [14–16]. Further neutron scattering studies showed a more complex picture, revealing several intermediate structural phases for H₂ and D₂ [17,18].

The diffusive dynamics of hydrogen/carbon systems have been studied intensely by means of quasi-elastic neutron scattering in recent years. The investigated carbon systems were varied, including graphite [19], single-walled carbon nanotubes (SWNTs) [20], carbon nanohorns [21], porous carbons [22–24], potassium intercalated graphite [25,26], and platinum containing porous carbon [27]. The latter carbon exhibited two diffusion processes with different time scales. Nguyen et al. observed different diffusion rates for H₂ and D₂ at low temperatures in a carbon molecular sieve [28].

The role of carbon substrates in the conversion from ortho- to para-hydrogen has also been the subject of numerous studies. An exhaustive review of research on the ortho-para conversion has been published by Ilicsa in 1992 [29]. The review focused on the different conversion channels that had been discussed theoretically, the main ones being paramagnetic and ferromagnetic interaction, as well as chemical dissociation at a metal surface. First measurements on the conversion were performed in 1929 [30]. In these first experiments, already, activated carbon helped to obtain a

* Corresponding author. Institut Laue-Langevin, CS 20156, F-38042 Grenoble Cedex 9, France.

** Corresponding author. Institut Laue-Langevin, CS 20156, F-38042 Grenoble Cedex 9, France.

E-mail addresses: bahn@ill.fr (E. Bahn), fouquet@ill.fr (P. Fouquet).

rapid ortho-para conversion. A systematic investigation of the activity of different substrates was performed in 1932 [31], where it was shown that the conversion mechanism on carbon, in contrast to metal substrates, involves a bi-molecular interaction. Neutron scattering on ortho- and para-hydrogen has been investigated theoretically [32,33] and experimentally [34–37]. Nuclear magnetic resonance (NMR) measurements of the conversion have been performed on solid hydrogen [38] and in the confined geometry of a zeolite adsorbate [39]. The latter study also showed a change in conversion rates. The conversion has been measured also in activated nanoporous carbon [23] and SWNTs [40]. While in both cases a rapid conversion was observed, Contescu et al. observed an incompleteness of the conversion that was suggested to be due to hindered rotations caused by narrow confinement in ultramicropores [23]. This assumption was corroborated by calculations of the dynamics of H₂ in SWNTs [41].

In the present paper, we study the adsorption, dynamics and ortho-para conversion of hydrogen in a carbon aerogel (CG) [42]. CGs have high specific surface area and their three-dimensional structure and electric properties can be tuned e.g. by addition of dopants [9]. The CG used in the present study serves us as a “standard” aerogel, which we aim to tune in future studies for different pore geometries and surface chemistry.

This paper is organised as follows: In section 2 we give a brief overview of the synthesis of this carbon aerogel and we describe the experimental methods. In section 3 we present and discuss the experimental results. We first show results from adsorption measurements on the carbon aerogel (sec. 3.1). We then discuss neutron and X-ray scattering results and their implications on the structure of the material (sec. 3.2). We finally present our findings on the ortho-para conversion of the hydrogen spin states (sec. 3.3) and on the diffusion of hydrogen in the material (sec. 3.4). The paper finishes with a concluding section that summarises the major results of the study.

2. Methods

2.1. Synthesis of the carbon aerogel

A detailed description of the preparation of the carbon aerogel is given elsewhere [42]. Briefly, resorcinol (R)-formaldehyde (F) hydrogel, with an R/catalyst ratio of 50 was prepared in a first step. After one week of curing the gels were supercritically dried according to the method described in Ref. [43]. The dry aerogel rods were converted into carbon aerogel by heat treatment in a high purity nitrogen atmosphere (99.996%, Linde) in a rotary quartz reactor at a temperature of 1173 K for 1 h in a 25 ml/min nitrogen flow.

2.2. Sample characterisation

Nitrogen adsorption/desorption isotherms were measured at 77 K with a Nova 2000e (Quantachrome) computer controlled surface area and pore size analyser. The apparent surface area, S_{BET} , was calculated using the Brunauer–Emmett–Teller (BET) model [44]. The total pore volume, $V_{0.95}$, was derived from the amount of vapour adsorbed at relative pressure 0.95, assuming that the pores are then filled with liquid adsorbate. The micropore volume, W_{0-DR} , and the adsorption energy, E_{DR} , were derived from the Dubinin–Radushkevich plot [45]. The pore size distribution in the micro- and mesopore regions was calculated using density functional theory [46]. Carbon dioxide and hydrogen adsorption/desorption isotherms were measured at 273 K with an Autosorb-1 surface area and pore size analyser and at 77 K with an Autosorb-1C (both from Quantachrome), respectively. Transformation of the

primary adsorption data was performed by the Quantachrome software ASiQwin version 3.0.

The submicroscopic structure of the carbon aerogel was explored by small and wide angle X-ray scattering (SAXS/WAXS) on the BM02-D2AM beamline at the European Synchrotron Radiation Facility (ESRF), Grenoble, France at 19.8 keV. The powdered sample was placed in a glass capillary tube of diameter 1.5 mm. The scattered intensity was collected in the wave vector transfer range $0.006 < q < 10 \text{ \AA}^{-1}$. Intensities were normalised with respect to a standard sample (Iupolen).

The elemental analyses of C, H, O, N and S were carried out in a LECO Truspec Micro CHNS microanalysis apparatus with a LECO Truspec Micro O accessory for O analysis. The amounts of C, H, S and N were determined from the amounts of CO₂, H₂O and NO₂ produced in the combustion of a portion of the sample (1 mg of sample was used for each assay, with two repetitions). The oxygen fraction was determined from the amounts of CO and CO₂ released in a pyrolysis at very high temperature, in a different portion of sample.

X-ray photoelectron spectroscopy (XPS) measurements were made on a powdered sample in a SPECS spectrometer with a Phoibos 100 hemispherical analyser. The base pressure in the UHV chamber was about 1.0×10^{-7} Pa. The X-ray radiation source delivered non-monochromatic Mg K α (1253.6 eV) at 100 W X-ray power and an anode voltage of 11.81 kV. The photo-excited electrons were analysed in constant pass energy mode, using a pass energy of 50 eV for the survey spectra and 10 or 30 eV for the high resolution core level spectra, respectively. Spectra were recorded at a take-off angle of 90°. No binding energy correction was done because the sample did not exhibit any charging effects. CasaXPS software was used for data processing.

2.3. Neutron scattering

Neutron time-of-flight (TOF) spectroscopy was performed on the backscattering spectrometer OSIRIS at the ISIS neutron source, UK [47], using a pyrolytic graphite (002) analyser set-up. The scattering functions from neutron TOF spectroscopy, $S(Q, \omega)$, where $Q = |\mathbf{k}_i - \mathbf{k}_f|$ is the momentum transfer and $\hbar\omega = E_i - E_f$ is the energy transfer, covered a momentum transfer range of $0.2 \leq Q \leq 1.8 \text{ \AA}^{-1}$ and an energy transfer range of $-0.2 \leq \omega \leq 1.0 \text{ meV}$. The data were grouped into windows with widths of $\Delta Q = 0.2 \text{ \AA}^{-1}$ and $\Delta\omega = 5 \text{ \mu eV}$ in momentum transfer and energy transfer, respectively. All OSIRIS data were extracted using the Mantid software package [48]. The instrument resolution function was measured with a vanadium sample and with the sample itself at the base temperature of the cryostat. The latter resolution function was used for the data interpretation to exclude the introduction of systematic errors caused by minor discrepancies between the scattering geometry of the vanadium and the sample. We note also that the elastic line of OSIRIS is not symmetric in energy and cannot be approximated easily by a smooth standard function.

The powdered carbon aerogel was filled into a hollow, cylindrical aluminium sample holder with an annular width of 1 mm. Prior to the neutron scattering measurements, the sample was out-gassed for 60 h in vacuum at a temperature of 393 K to remove volatile contaminants from the surface. The temperature was controlled using a standard liquid helium cryostat (“orange” cryostat [49]). For the neutron scattering experiments the sample was first cooled to 1.7 K in order to obtain an elastic scattering resolution measurement of the clean carbon sample. Afterwards, the sample was heated to 20 K and the quantity corresponding to 0.5 ML of hydrogen gas was dosed through a stainless steel capillary that was connected to a pressure control monitor. The hydrogen coverage was calculated from the amount of injected hydrogen

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