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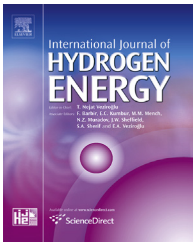

Hydrogen uptake of high surface area-activated carbons doped with nitrogen

W. Zhao [a,b,c], V. Fierro [a,*], N. Fernández-Huerta [d], M.T. Izquierdo [d], A. Celzard [a,b,1]

[a] Institut Jean Lamour, UMR CNRS 7198, ENSTIB, 27 rue Philippe Séguin, CS 60036, 88026 Epinal Cedex, France
[b] Université de Lorraine, ENSTIB, 27 rue Philippe Séguin, CS 60036, 88026 Epinal Cedex, France
[c] College of Material Engineering, Fujian Agriculture & Forestry University, Fuzhou, Fujian 350002, China
[d] Instituto de Carboquímica (ICB-CSIC), Miguel Luesma Castán, 4, 50018 Zaragoza, Spain

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ABSTRACT

Three activated carbons (ACs) having apparent surface areas higher than 2500 m^2/g were doped with nitrogen by treatment with urea at 623 K under air flow. Nitrogen contents as high as 15.1 wt.% were obtained, but resulting in decreased surface areas and pore volumes. Hydrogen storage capacities of ACs before and after nitrogen doping were measured at 77 K and up to 8 MPa. After doping, the hydrogen uptake was lower due to the corresponding decrease of surface area. Statistical, ANOVA, analysis of the relevancy of surface area and nitrogen content on hydrogen storage at 77 K was carried out, taking into account our data and those data available in the open literature. We concluded that surface area controls hydrogen adsorption and nitrogen content is not a relevant parameter.

1. Introduction

The US Department of Energy (DOE) set three goals for hydrogen storage systems to be used for automotive applications, which are reversibility, gravimetric density around 6 wt.% [1], and heat of adsorption (ΔH_{ads}) within the 20–30 kJ/mol range [2,3]. High surface area activated carbons (ACs) with optimal pore sizes around 0.5–0.7 nm have been suggested [4–6] as potential candidates to reach high hydrogen storage capacities at 77 K. If high surface area is indeed necessary, it is not the only requirement and we have shown that an appropriate pore size distribution is also needed. Thus, H_2 uptakes higher than 3 wt.% at 77 K are due to pores having diameters wider than 0.7 nm [7,8] in ACs prepared from KOH activation. Even if surface area and pore size distribution were optimized, we have experimentally shown that a maximum of hydrogen adsorption on ACs exists [9], and this maximum is very close to the 6.6 wt.% calculated by Schlapbach and Züttel [10].

The typical energy contribution from dispersive forces to hydrogen adsorption in porous solids such as ACs is roughly 6 kJ/mol, and remains well below the lower limit for the ideal ΔH_{ads} range (20–30 kJ/mol). A possible strategy for increasing the strength of the gas–solid interaction, and hence the hydrogen storage capacity of ACs, is the introduction of metal nanoparticles or heteroatoms in the carbon matrix [11]. Thus, doping ACs with Pd nanoparticles was tested as a method for improving hydrogen storage by spillover [12–16]. However, as hydrogen storage on high surface area-ACs at 77 K primarily

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[*] *Corresponding author*. Fax: +33 329 29 61 38.
E-mail address: Vanessa.Fierro@lcsm.uhp-nancy.fr (V. Fierro).
[1] Member of the Institut Universitaire de France.

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depends on microporosity, Pd doping may decrease the micropore volume available for adsorption and hence the hydrogen storage capacities [17].

Introduction of heteroelements significantly alters the electronic structure of the carbon matrix, thus affects the interactions between solid carbon and adsorbed hydrogen and might increase the amount of hydrogen stored. Promising results were obtained by introducing boron [18], silicon [19], sulphur [20] or nitrogen [21] into carbon. Nitrogen doping has been studied more extensively than the other heteroatoms, but contradictory results were reported in the literature. Zhou et al. [22] studied, through density functional theory (DFT) calculations, the effect of N-doping on hydrogen adsorption on single-walled carbon nanotubes. They found that N-doping decreased the hydrogen molecular adsorption energies. Kang et al. [23] found that hydrogen adsorption at 77 K was more strongly related to specific surface area than to nitrogen content. Xia et al. [24] found that N-doping can be beneficial at low hydrogen uptake but is detrimental at high hydrogen uptake. Wang et al. [25,26] prepared nitrogen-doped ACs and found that hydrogen storage in such samples was much higher than that of non-doped materials of similar surface area. Finally, other studies concluded that nitrogen doping has no impact on hydrogen storage [27–29].

Therefore, the effect of nitrogen doping on hydrogen storage is still debated and, most of times, it is difficult to separate the combined effects of porosity and chemical composition. In the present manuscript, we doped three high surface area ACs, resulting in materials with nitrogen contents as high as 15.1 wt.%. Hydrogen storage capacity of raw and N-doped ACs was measured at 77 K, and our results were compared to those reported in the open literature.

2. Experimental

2.1. Materials synthesis

The ACs' precursor was Chinese anthracite from Taisi mine, with an average particle size within the range 100–200 μm. ACs were prepared by chemical activation with KOH, as described elsewhere [9,30]. Nitrogen doping was then carried out by physical mixing of urea and AC, using urea to AC weight ratios of either 1 or 2, followed by thermal treatment in a horizontal furnace under air flowing at 50 cm^3/min. Temperature was increased at 5 K/min up to 623 K, the final temperature was maintained for 3 h, then the furnace was allowed to cool down to room temperature under air flow. The N-doped ACs were finally washed with hot water until neutral pH in a Soxhlet extractor, and dried.

2.2. Physicochemical characterization

2.2.1. Nitrogen content determination

Nitrogen content was determined by elemental analysis (EA) and X-ray photoelectron spectroscopy (XPS). EA was carried out in a ThermoFlash 1112 apparatus to determine carbon, hydrogen, nitrogen and sulphur contents. Oxygen content was obtained by difference. XPS spectra were recorded with an ESCAPlus OMICROM system equipped with a hemispherical electron energy analyzer. The spectrometer was operated at 10 kV and 15 mA under vacuum ($<7 \times 10^{-7}$ Pa), using a non-monochromatised Mg Kα X-Ray Source ($h\nu = 1253.6$ eV). Analyzer pass energies of 50 and 20 eV were used for full and detailed scans, respectively. The C1s peak at 284.5 eV was used for binding energy correction.

2.2.2. Nitrogen physisorption

Nitrogen adsorption–desorption isotherms were obtained at 77 K using a Micromeritics ASAP 2020 automatic apparatus. The samples were degassed for 48 h under vacuum at 523 K prior to any adsorption experiment. Nitrogen adsorption data were obtained and treated as described elsewhere [9,30] for obtaining: (i) apparent surface area, S_{BET}, by the BET calculation method [31]; (ii) micropore volume, V_{DR}, according to the Dubinin–Radushkevich (DR) method [32] and refs. therein; (iii) total pore volume, $V_{0.99}$, defined as the volume of liquid nitrogen corresponding to the amount adsorbed at a relative pressure $P/P_0 = 0.99$ [33]. The mesopore volume, V_{me}, was calculated as the difference $V_{0.99} - V_{DR}$. The average micropore diameter, L_0, and adsorption energy, E_a, were also calculated [34], as well as the pore size distributions (PSD) by application of the Density Functional Theory (DFT) [35].

2.2.3. Hydrogen storage

Adsorbed hydrogen uptake at 77 K was measured with a gravimetric analyzer (VTI Corporation). Hydrogen isotherms were obtained by setting pressure steps within the range 0–8 MPa at 77 and 298 K. More details are given elsewhere [9,30]. The counterpart excess hydrogen isotherms were measured in a volumetric device (HPVA-II, Micromeritics) in the same conditions.

3. Results and discussion

3.1. Materials composition

3.1.1. Elemental analysis

All ACs, non-doped and N-doped, were labelled ACxx'y. In such nomenclature, x and x' correspond to the first two digits of the value of S_{BET} for the non-doped AC (N-doped AC precursor), whereas y is the weight ratio of urea to AC: 0 for non-doped ACs, and either 1 or 2 for N-doped ACs. For example, AC250 is a raw AC having a S_{BET} of 2500 m^2/g, whereas AC251 is the N-doped counterpart prepared from AC250 using an urea/AC weight ratio (W) of 1.

Table 1 shows the results of elemental analysis of all studied ACs. Nitrogen content of raw materials was very low, typically ranging from 0.2 to 0.3 wt.%, whereas that of N-doped ACs was between 7.8 and 15.1 wt.%. Materials prepared from ACs having S_{BET} of 2527, 2955 and 3434 m^2/g with W = 1 had nitrogen contents of 7.8, 9.9 and 8.8 wt.%, respectively. Using W = 2 in the AC30y series, the N content increased from 9.9 to 15.1% and C content decreased from 85.3 to 80.2%, whereas H and O contents remained roughly constant. These results seem to indicate that the amount of nitrogen in the final product not only depends on the oxygen content of the precursor, as concluded by Pietrzak et al. [36], but also on the value of W. As a result of N-doping treatment in the AC30y

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