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Assessment of hydrogen storage in activated carbons produced from hydrothermally treated organic materials

S. Schaefer ^{*a,b*}, V. Fierro ^{*a,b,**}, M.T. Izquierdo ^{*c*}, A. Celzard ^{*a,b*}

^a Université de Lorraine, ENSTIB, 27 Rue Philippe Séguin, CS 60036, 88026 Épinal Cedex, France ^b Institut Jean Lamour, UMR CNRS 7198, ENSTIB, 27 Rue Philippe Séguin, CS 60036, 88026 Épinal Cedex, France ^c Instituto de Carboquímica: Miguel Luesma Castán, 4, Zaragoza E-50018, Spain

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ABSTRACT

12 activated carbons (ACs) were prepared by KOH activation using hydrochars as precursors. These hydrochars were prepared by hydrothermal carbonisation (HTC) of sucrose solutions at concentrations ranging from 0.2 to 1.6 mol L⁻¹. The KOH to hydrochar weight ratio (W) was varied from 1 to 5, and the activation temperature was set to 1023 K. ACs texture was assessed by nitrogen and carbon dioxide adsorption at 77 and 273 K, respectively; pore size distribution was calculated by using both isotherms and the SAIEUS© software. ACs with surface areas between 790 and 2240 m² g⁻¹ were obtained. Hydrogen excess adsorption was determined at 298 K and pressures up to 10 MPa in a volumetric device, and the isosteric heat of adsorption (Q_{st}) was calculated for four ACs, using hydrogen isotherms obtained at 278, 298 and 308 K. Potassium intercalation between graphitic planes was assumed to account for the high Q_{st} values, 7–8 kJ mol⁻¹. Hydrogen uptake at 2 MPa was compared with hydrogen adsorption data of 38 other ACs reported in the open literature. Hydrogen adsorption fundamentally depends on micropore volume and preliminary HTC did not enhance hydrogen storage although it could be a good strategy for doping carbon with heteroelements.

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Introduction

Hydrogen is an energy vector which should be extensively used in the future. Storing energy by generating hydrogen during electricity production peaks might be a complementary alternative to the establishment of regulated energy networks like Smartgrids [1]. Several pilots plants, such as the MYRTE demonstrator in France, are converting solar energy into electricity, then into hydrogen, and they have already proved their efficiency [2].

Hydrogen storage at high pressure or in liquid state is controversial due to security issues that also imply social acceptability [3,4]. Hydrogen adsorption on a solid surface allows reducing the storage pressure but requires low temperatures to enhance adsorption capacity. However, hydrogen

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^{*} Corresponding author. Université de Lorraine, ENSTIB, 27 Rue Philippe Séguin, CS 60036, 88026 Épinal Cedex, France. Tel.: + 33 329 29 61 77.

E-mail address: Vanessa.Fierro@univ-lorraine.fr (V. Fierro). http://dx.doi.org/10.1016/j.ijhydene.2016.05.086

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storage at moderate pressures, lower than 4 MPa, and at room temperature remains a challenge. The theoretical upper limit for hydrogen storage in carbon materials is around 6.9 wt.% at 77 K [5], and such value was already experimentally attained with some activated carbons [6–8]. This value is higher than the 5.5 wt% recommended by the DOE for automotive applications in 2017.

Nevertheless, not only the weight of the storage material but that of the entire system has to be taken into account. Therefore, 5.5 w% of the adsorbent weight is not enough. Moreover, the DOE recommends meeting such capacities in the 233–358 K temperature range, whereas the aforementioned values were measured at 77 K [9]. Still, lower capacities can be accepted for stationary applications, for which volume and weight are not limiting factors. As a consequence, the search for carbon materials able to store hydrogen at room temperature remains a hot topic nowadays. Activated carbons produced by KOH activation after a previous hydrothermal carbonisation (HTC) step of a variety of organic materials (saccharides, biomass or furfural) exhibited high hydrogen uptakes at 77 K, up to 6.4 wt.% and high isosteric heat of adsorption, between 6 and 8.5 kJ mol⁻¹ [10].

Researches on HTC and on other treatments in pressurised hot water started at the beginning of the 20th century [11–13]. HTC is the thermal treatment of a carbon precursor, whether natural or not, in water under moderate temperature and selfgenerated pressure in an autoclave. The latter induces both reaction and nucleation processes [14]. HTC occurs typically in the range 403-523 K, and the recovered materials are called hydrothermal carbons or hydrochars [15]. Most of the times, when a solution is submitted to HTC hydrochars present a microsphere-like morphology [16-18] that sometimes remains after KOH activation [16–18]. Many organic precursors were treated by HTC to produce carbon materials, e.g. starch, sawdust, glucose, tannins, chitosan or glucosamine [10,16,19,20]. When carbohydrates are involved, HTC proceeds by hydrolysis and intramolecular dehydration and polycondensation of the hydrolysis products [11]. These reactions lead to the formation of amphiphilic macromolecules forming micelles, which nucleate by dehydration and grow via a diffusion process [14]. Increasing the initial concentration of the carbonaceous precursor in the solution induces the increase of the average microsphere diameter [14,16].

HTC is also an interesting method to produce carbons doped with heteroatoms such as nitrogen. Thus, nitrogen-rich carbonaceous materials were synthesised from tannin submitted to HTC in concentrated ammonia [21]. These materials can be carbonised and physically or chemically activated to obtain carbon materials with high and tuneable porosity for specific applications [18,21,22]. Indeed, according to several authors, these materials have a high potential for gas sorption and especially for carbon dioxide or hydrogen adsorption [23,24]. The objective of the present study was to provide unquestionable proofs or rebuttals of the beneficial effect of a hydrothermal pre-treatment to synthetize activated carbons for hydrogen storage. For this purpose, hydrochars were produced by submitting sucrose solutions to HTC and these hydrochars were further activated with KOH. We studied the effect of both the initial sucrose concentration and the ratio KOH/hydrochar on the textural properties of the resultant activated carbons (ACs), and hence on their hydrogen storage performances. Our results were compared with those reported in the open literature.

Experimental

Preparation of hydrochars

Sucrose of purity 99%, supplied by Sigma Aldrich[®], was used as precursor. Sucrose solutions were prepared at different concentrations in bi-distilled water, namely: 0.2, 0.4, 0.8 and $1.6 \text{ mol } \text{L}^{-1}$.

HTC reactions were carried in 125 cm³-capacity Teflonlined autoclaves supplied by Parr Instrument Company[®] under reference "Large Capacity Acid Digestion Vessel – Model 4748". To avoid contamination of the Teflon pot during the synthesis, the sucrose solution (30 cm³) was poured into a glass insert fitting the dimensions of the Teflon pot. Doing this, the available inner volume of the autoclave decreased to 100 cm³. The oven was preheated at 453 K and once the temperature was constant, the autoclaves were introduced in the oven and left for 24 h. After thermal treatment, the autoclaves were cooled and the solutions were filtrated to recover the solid fraction, i.e. the hydrochar, which was dried in a vacuum oven at 353 K and 15 kPa overnight.

Activation

Hydrochars were carbonised and activated in a single stepprocess using potassium hydroxide (KOH) as activating agent. KOH lentils and hydrochars were ground together in a weight ratio KOH to hydrochar (W) ranging from 1 to 5, and the resultant blends were put in a nickel crucible placed inside the stainless steel reactor of a tubular oven. The tube length was 1.20 m and its inner diameter was 0.12 m. A heating rate of 3 K min⁻¹ was applied up to the final temperature, 1023 K, which was maintained for 1 h. The oven was continuously flushed by a 70 cm³ min⁻¹ nitrogen flow during the whole activation process: heating, plateau and cooling.

After activation, the obtained activated carbons (ACs) were washed with a 0.1 mol L^{-1} solution of hydrochloric acid, then with bi-distilled water, and finally were thoroughly washed in a Soxhlet extractor with water for 3 days. For that purpose, the ACs were put in dry cellulose cartridges of know weights before putting them in the Soxhlet. Finally, the cartridges were dried in a ventilated oven at 378 K and weighed for calculating the AC yield (Y_{AC}) determined as:

$$Y_{AC} = rac{activated \ carbon \ (g)}{precursor \ (g)} imes 100$$

where precursor stands for hydrochar when HTC was used or, sucrose or pyrolysed sucrose as we will see afterwards.

The samples were labelled AcHTC_M_W, where "Ac" means that the material was activated, "HTC" has the same meaning as before, "M" (molarity) stands for the concentration of the initial solution, and "W" is the activation ratio. Labels comprising neither "Ac" nor W values correspond to hydrochars, i.e. to non-activated materials. For instance

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