Chitosan-based highly activated carbons for hydrogen storage

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ABSTRACT

Highly microporous activated carbons (ACs) were prepared using chitosan, a low cost and abundant biopolysaccharide, as a carbon precursor. Chitosan chars were activated with KOH in different experimental conditions, yielding chitosan-based ACs with high surface areas (922–3066 $m^2\ g^{-1}$) and pore volumes (0.40–1.38 $cm^3\ g^{-1}$). Microporosity was the main contributor to the total pore volume for all ACs. Chitosan-based ACs were tested as hydrogen storage systems using hydrogen physisorption at atmospheric pressure and 4 MPa. The optimized ACs exhibited excellent hydrogen adsorption capacities at 77 K (2.95 wt% at 0.1 MPa, 5.61 wt% at 4 MPa). Micropores with a width of 0.7–1 nm were mainly responsible for hydrogen adsorption at atmospheric pressure, whereas larger pores did not exert any noticeable influence. Conversely, the presence of supermicropores and small mesopores also enhanced hydrogen uptake at 4 MPa. These results show a high potential for the use of chitosan-based ACs in hydrogen storage systems.

Introduction

Currently, the high reliance on fossil fuels as the primary energy source and the environmental impact derived from their use are major concerns worldwide. The development of a hydrogen-based economy is one of the emerging strategies to reduce the use of fossil fuels. Hydrogen holds the highest energy density by weight among fuels (33.59 kWh kg^{-1}) and is considered an appealing emissions-free substitute for hydrocarbons in stationary (residential) and non-stationary (automotive) applications [1]. The main drawback of hydrogen as an energy vector is its low energy density by volume, arising from its very low density (90 g m^{-3} at 0.1 MPa and 273 K). For

this reason, research is being done on developing feasible hydrogen storage systems based on compression, liquefaction, adsorption in microporous materials or in the form of metal hydrides [2].

Activated carbons (ACs) have been extensively studied as hydrogen storage materials because of their high surface area, low density and chemical stability. Although hydrogen adsorption in ACs at ambient temperature is relatively low even at high pressures [3–5] due to the low quadrupole moment and the low polarizability of the H_2 molecule [4], hydrogen cryosorption is considered to be a promising method for hydrogen storage, as ACs can reversibly adsorb substantial quantities of hydrogen with fast adsorption/

desorption kinetics [6,7]. The porous texture is the main feature determining the hydrogen adsorption capacity of ACs. Some authors have stated that ACs should have a highly developed internal surface and a large volume of micropores [8,9] with diameters in the range of 0.6–0.8 nm [6,8,10–12] for an efficient performance as a hydrogen storage material at both atmospheric and high pressures. Obtaining very high surface areas often leads to increasing pore sizes, which limits the hydrogen storage capacity of these materials [2,13]. However, other authors have noted that the presence of larger pores provides higher hydrogen adsorption capacities [3,14,15].

Porous carbons can be prepared from different carbon precursors, including wood, peat, coal, coconut and fruit stones and polymers, by physical and chemical activation methods. In particular, chemical activation with KOH leads to microporous ACs with very high surface areas (>2500 $m^2 g^{-1}$) and high yields [16] and requires lower pyrolysis temperatures than physical activation. The nature of a carbon precursor, its carbonization degree, the activation temperature and the amount of activating agent used are the main factors determining the porosity development during activation with KOH [17–19].

Among all the precursors suitable for the preparation of ACs, natural and synthetic polymers are promising because of their high carbon yield and low ash content. Chitosan is a biopolysaccharide obtained by N-deacetylation of chitin, which is naturally abundant in the exoskeleton of crustacean shells. Given that more than 1300×10^6 tons of chitin per year are obtained as byproducts in the food industry [20], the preparation of chitosan from readily available shell waste is economically feasible and environmentally friendly [21]. The chemical structure of chitosan is similar to that of cellulose, but with amino groups in the place of hydroxyl groups at the C-2 positions (Fig. 1). Due to its special physical, chemical and biological properties, chitosan is extensively used in the food industry, agriculture, medicine and water treatment [21]. Nevertheless, few works have described the transformation of chitosan into porous carbons using Na_2CO_3 [22], K_2CO_3 [23] or $ZnCl_2$ [24] as activating agents. To the best of our knowledge, the activation of chitosan using metal hydroxides such as KOH has not been reported.

In this work, we studied the synthesis of chitosan-based ACs with a highly developed microporous structure by a chemical activation process using KOH as an activating agent. The effect of different carbonization and activation conditions on the porous structure of the ACs was investigated in detail. We assessed the behavior of chitosan-based ACs in hydrogen adsorption at 77 K and the influence of the porous structure on their hydrogen adsorption capacity, both at atmospheric pressure and at 4 MPa.
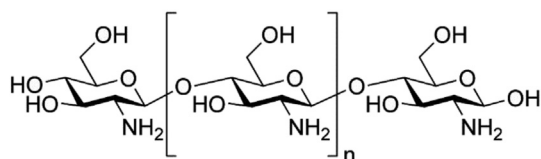

Fig. 1 – The chemical structure of chitosan.

Experimental

Synthesis and characterization of chitosan-based ACs

Chitosan (1500 amu) from Sigma–Aldrich was used as the AC precursor. Prior to activation, chitosan was carbonized in a horizontal furnace. Ten grams of chitosan was placed in a quartz boat and heated to 700, 800, 900 and 1000 °C at a heating rate of 10 °C min^{-1} under nitrogen flow (10 $dm^3 h^{-1}$). The soaking time at the final temperature was 30 min. The char was physically mixed with anhydrous KOH using KOH/char ratios (wt/wt) ranging from 1 to 4 and activated in a horizontal furnace. Each mixture was placed in a nickel boat and heated to 700 and 800 °C for 1 h with a heating rate of 10 °C min^{-1} under a nitrogen flow of 30 $dm^3 h^{-1}$. The resultant ACs were washed repeatedly with 5% HCl and distilled water to remove chloride ions and dried in an oven at 110 °C for 12 h. Samples were labeled as ChX/Y/Z, where X is the carbonization temperature, Y is the activation temperature and Z is the KOH/char ratio.

The porous texture of the ACs was determined by nitrogen physisorption at 77 K in an ASAP 2020 Micromeritics apparatus. The samples were previously outgassed at 300 °C for more than 12 h. The specific surface area (S_{BET}) was calculated from the isotherm data using the BET (Brunauer, Emmett and Teller) method. The amount of nitrogen adsorbed at the relative pressure of $p \ p_0^{-1} = 0.96$ was used to determine the total pore volume (V_T). The micropore volume (V_{DR,N_2}) and the average micropore width (L_0) were estimated by applying the Dubinin-Radushkevitch and Stoeckli equations to data collected at low relative pressures ($p \ p_0^{-1} < 0.015$) [25]. Pore size distributions were also calculated from the isotherm data by applying the Quenched-Solid Density Functional Theory method (QSDFT) [26].

Hydrogen adsorption measurements

The hydrogen storage capacity at 77 K was evaluated both at atmospheric pressure and at 4 MPa. Measurements at atmospheric pressure were carried out in a NOVA2200 (Quantachrome) apparatus. Prior to these measurements, 0.25 g of each sample was outgassed overnight at 300 °C. Hydrogen uptake under higher pressure (up to 4 MPa) was determined using a homemade Sievert-type volumetric apparatus. Prior to the measurement, 0.8–1.0 g of the sample was outgassed at 300 °C for 1 h. Two measurements of hydrogen sorption at atmospheric pressure and at high pressure were performed for each sample.

Results and discussion

Structural characterization of chitosan-based ACs

ACs were prepared from chitosan by pre-carbonization and chemical activation with KOH. The carbonization yield varied from 31 wt% at 700 °C to 29 wt% at 1000 °C. It is well known that the carbonization and activation temperatures, as well as the amount of the activating agent, determine the textural