Activated carbon with optimum pore size distribution for hydrogen storage

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A B S T R A C T

A series of nitrogen containing activated carbons (NAC-1.5-y) with surface areas and pore volumes in the range of 526–2386 m^2/g and 0.26–1.16 cm^3/g, respectively were prepared by treatment of a nitrogen-rich carbon with KOH (KOH to carbon weight ratio = 1.5) at different temperatures (y) in the range of 550–700 °C. The prepared samples were used to delineate the role of pore sizes and nitrogen content in hydrogen adsorption at 77 K. The activated carbons showed high hydrogen uptake, due to increased porosity (>0.364 nm). The optimized carbon material NAC-1.5-600, with high nitrogen content (22.3 wt %) and large volume of ultra-micropore centered at 0.59 nm in size, showed hydrogen uptake of 2.94 wt% at 77 K and 1 bar. The adsorption capacity was found to be linearly dependent on ultra-micropore volume (0.5–0.7 nm), but not linearly associated with the total surface area nor the total pore volume. Nonetheless, the surface area of larger pore material (NAC-1.5-700) was found to be favorable for hydrogen adsorption at high partial pressure. The data obtained indicated that the occurrence of nitrogen, oxygen and hydrogen-containing species has hardly any effect on hydrogen uptake at 77 K.

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1. Introduction

The decreasing oil reserves and growing environmental awareness created the need for more eco-friendly fuels and zero emission vehicles. Hydrogen as an alternative to fossil fuel, has been recognized as an attractive energy carrier for both stationary and locomotive applications. Although hydrogen has the highest gravimetric energy density of 120 kJ/g, about three times the energy density of gasoline, and it does not generate any greenhouse gas emissions upon oxidation, the on-board storage of hydrogen is still a major challenge [1,2]. The US Department of Energy set the goal of 5.5 wt% gravimetric reversible hydrogen storage, for systems to be used in automotive applications [3,4]. To a large extent the success of on-board hydrogen storage applications rests on the development of efficient, low-cost materials, including adsorbents with high reversible uptake and stability [5].

Many hydrogen storage methods including physisorption, chemisorption, spillover, metal hydrides, liquid hydrogen, and high-pressure hydrogen have been proposed for hydrogen storage.

However, they are still far from large-scale implementation due to economic and/or technical challenges [4,5]. Hydrogen adsorption in porous materials offers several advantages over other methods, namely, fast adsorption and desorption kinetics, no need for energy to release hydrogen, and high hydrogen uptake at low temperature and moderate pressures. Among the various adsorbents like metal-organic frameworks (MOFs), zeolites and others, carbon materials offer many advantages such as heat resistance, chemical stability, reversibility, low-cost and availability [6–8]. Additionally, light-weight carbons with large porosity are a preferred choice to achieve the gravimetric hydrogen storage target.

Various carbon materials for hydrogen adsorption have been reported, including activated carbons (AC), carbon aerogels, graphene, and carbon nanotubes [1,9–11]. Despite several advantages of carbon materials, the main drawback that may limit their application in hydrogen storage is their low heat of adsorption. The optimum heat of adsorption required for maximum delivery at 298 K is 15.1 kJ/mol [12]. Poorly-polarizable hydrogen molecules adsorb on the surface of carbons by weak van der Waals forces. Therefore, the narrower the pores, the stronger the hydrogen-to-surface interactions, and the higher the adsorption capacity. Hence, among the many proposed carbons, materials with ultra-microporosity are of significant importance in hydrogen storage due to their enhanced heat of adsorption [13].

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Recently, a number of microporous carbon materials based on natural and synthetic precursors were found to exhibit excellent hydrogen adsorption capacity (Table 1) [14—20]. The organic precursors were transformed into porous activated carbons by carbonization followed by KOH activation. To the best of our knowledge the highest hydrogen uptakes at 77 K and 1 bar reported for any natural and synthetic material-derived AC are 3.28 wt% from hemp stem [20] and 2.85 wt% from petroleum pitch [15].

Among the wide range of pore sizes in carbon materials, several researchers stressed the importance of small micropores ($\leq$1 nm) and showed that such pores are efficient for hydrogen storage, whereas pores above 1 nm do not contribute much toward hydrogen adsorption at 77 K [13,21—26]. Both experimental and theoretical studies suggested that pores with 0.5—0.7 nm width are ideal for hydrogen adsorption at 77 K due to the overlap of potential fields from both sides of the pore walls [13,21—26]. Adsorption is a surface phenomenon and it is obvious that the surface composition, particularly the nitrogen content may play an important role in the hydrogen adsorption by activated carbons. Nonetheless, recent reports regarding the role of surface composition in hydrogen adsorption are contradictory [15,26—32]. Taking into account the data available in the literature, and considering the importance of micropore volume and surface area from pores with 0.5—0.7 nm diameter, and the conflicting findings regarding the effect of surface composition on hydrogen adsorption at 77 K, we successfully optimized the carbon activation procedure and developed strictly microporous AC materials with high nitrogen content, and large volume from pores around 0.59 nm wide for ultra-high hydrogen uptake. The effects of ultra-micropores and chemical composition were discussed in light of the experimental data obtained.

2. Experimental

2.1. Materials

Trimethylsilyl imidazole and chloroacetonitrile were obtained from Alfa Aesar, hydrochloric acid (38 wt%), ammonia (28 wt%) and potassium hydroxide were purchased from Sigma—Aldrich. Hydrogen (99.999%), nitrogen (99.9993%), and helium (99.999%) were supplied by Linde Canada.

2.2. Synthesis of activated carbons

A three-step method was used for the preparation of activated carbons, starting by the synthesis of carbon precursor (CP). The CP was synthesized using a reported procedure [33]. A mixture of trimethylsilyl imidazole (4.6 g) and chloroacetonitrile (4.9 g) was stirred at room temperature for 24 h under inert atmosphere to form 1,3 bis(cynomethyl imidazolium) chloride, a white solid material. This material was washed with diethyl ether and dried under vacuum before further use as carbon precursor. The second step

was a carbonization process. The white solid was placed in an alumina boat, transferred into a tubular furnace and then heated under N_2 flow (100 cm^3/min) at a rate of 10 °C/min, with a holding time of 2 h at the final temperature. Materials obtained after carbonization at 400 and 600 °C were named as CP-400 and CP-600, respectively. The last step was an activation process to generate porosity in the carbonized material. The activation procedure was reported elsewhere [34]. Briefly, the non-porous CP-400 material (*vide infra*) was thoroughly mixed with KOH (KOH/CP-400 weight ratio 1.5) and heated under N_2 flow (100 cm^3/min) at a rate of 3 °C/min up to a temperature in the range of 550—700 °C, and held at the final temperature for 1 h. The activated samples were then thoroughly washed and dried in an oven at 80 °C overnight. The activated carbons thus synthesized were denoted as NAC-1.5-*y*, where NAC stands for nitrogen-doped activated carbon, 1.5 is the KOH/CP-400 weight ratio and *y* is the activation temperature in °C.

2.3. Characterization

The textural properties of the synthesized AC materials were determined based on nitrogen adsorption/desorption measurements at 77 K using a Micromeritics ASAP 2020 apparatus. The surface area was calculated using the BET method within the relative pressure (P/P_o) range of 0.05—0.20. The total pore volume was determined from the amount of nitrogen adsorbed at P/P_o as close as possible to 1. The pore size distribution (PSD) was determined using the density functional theory (DFT) model with slit pore geometry. The carbon, nitrogen, hydrogen contents of the carbon samples were determined by elemental analysis using a Vario EL III instrument. The surface analysis was achieved by X-ray photoelectron spectroscopy (XPS) using a Kratos Axis Ultra spectrometer. More details may be found elsewhere [34]. Transmission electron microscopy (TEM) images were taken using a JEOL JEM-2100F instrument.

2.4. Hydrogen adsorption measurements

Hydrogen adsorption isotherms were measured at 77 K using a static volumetric system (ASAP 2020). The hydrogen adsorption capacity, as weight percent of hydrogen adsorbed per gram of adsorbent, was determined from the adsorption isotherms. Prior to adsorption measurements, the samples were activated *in situ* by heating under vacuum at 200 °C for several hours to remove the adsorbed moisture and clean the surface.

3. Results and discussion

Fig. 1 shows the nitrogen adsorption/desorption isotherms of the prepared carbons. All AC samples exhibited type I isotherms according to the IUPAC classification. The non-activated carbons

Table 1
Hydrogen storage at 77 K and 1 bar over KOH-activated carbons derived from natural and synthetic precursors.

Activated carbons	Precursor (natural/synthetic)	H$_2$ uptake (wt%)	Reference
NAC-1.5-600[a]	1,3 bis(cynomethyl imidazolium) chloride	2.96	This work
ACT-850	Polythiophene	2.41	[14]
PBA	Petroleum residue	2.84	[15]
CAC1	Corncob	2.85	[16]
Ch800/700/3	Chitosan	2.95	[17]
C2-1/4-700	Cellulose	2.50	[18]
CAC4	Corncob	3.21	[19]
AC8[b]	Hemp stem (Cannabis sativa L.)	3.28	[20]

[a] Highest reported hydrogen uptake for any activated carbon derived from synthetic materials.
[b] Highest reported hydrogen uptake for any activated carbon derived from natural materials.