STUDY OF H$_2$ STORAGE PERFORMANCE OF PHYSICALLY ACTIVATED CARBON NANOFIBRES

M. Kunowsky[a], J.P. Marco-Lozar[a], A. Oya[b],
A. Linares-Solano[a]*

[a] Dpto. Química Inorgánica, Universidad de Alicante, Ap-99. E-03080 Alicante, Spain
[b] Department of Materials Science, Gunma University, Gunma, Japan
* linares@ua.es

Introduction

Recently, a novel kind of carbon nanofibers (CNFs), produced by polymer blend technique, has been used for producing highly nanoporous adsorbents [1,2]. In difference to CNFs synthesized by other methods, these CNFs feature a highly amorphous structure which substantially favours their activation [1]. In a previous study, these nanofibres were activated physically with H$_2$O, resulting in activated carbon nanofibres (ACNFs) with high surface areas up to 2000 m^2/g [2]. However, very low activation yields of only 6 wt.% were reached. In another study, their chemical activation with hydroxides was studied [1]. Highly microporous adsorbents were obtained with significantly higher yields. However, the chemical activation process is somewhat more laborious and costly than physical activation.

In the present study, we have studied the physical activation of these polymer blend CNFs with CO$_2$. We show that by such activation process, highly microporous ACNFs can be obtained with a reasonable high yield. Morphology and textural properties of the produced materials are studied, and their application as hydrogen storage materials is investigated. Additionally, due to the promising results and the high compressibility of the ACNFs, monoliths are produced in order to increase the storage density under practical conditions.

Experimental

The basics of the carbon nanofibre's preparation process were previously reported [2]. Physical activation of the CNFs with CO$_2$ was performed in a horizontal tube furnace. Firstly, the nanofibres were heated under a N$_2$ flow of 100 ml/min with a rate of 20ºC/min. Upon reaching the activation temperature of 825ºC, the flow was switched to CO$_2$ (100 ml/min). Different activation times of 12, 24, and 32 hours were used. Detailed descriptions of the CNF activations with hydroxides and steam can be found elsewhere [1,2]. The unactivated precursor is denominated CNF. The denomination of the activated samples follows the form CNF-[activating agent]-[activation time in h], whereby CD signifies carbon dioxide, S steam, Na sodium hydroxide, and K potassium hydroxide.

From ACNFs which were activated with CO$_2$ for 24 h, a monolith was produced. Therefore, the ACNFs were mixed with a 55 % aqueous solution of polymeric binder (Waterlink Sutcliffe Carbons) in a 1:1 binder-to-fibre ratio. The mixture was dried, compressed, and heated up to 140ºC. Finally, the resulting monolith was carbonised for 2 h at 750ºC. A detailed description of the procedure can be found in Ref. [3].

Isotherms of physical adsorption at sub-atmospheric pressures were measured for N$_2$ (99.999 %) at 77 K, for CO$_2$ (99.98 %) at 273 K, and for H$_2$ (99.999 %) at 77 K. The measurements were performed in two different kinds of volumetric adsorption apparatus, ASAP 2020 (Micromeritics), and Autosorb-6 (Quantachrome). Before the measurements, the samples were degassed at 523 K under vacuum for at least 4 h. From N$_2$ adsorption isotherms, the apparent BET surface area, S$_{BET}$, was obtained, and the total micropore volume, V$_{DR}$(N$_2$), was calculated according to the Dubinin–Radushkevich (DR) equation. The DR equation was also applied to CO$_2$ adsorption isotherms, in order to determine the volume of narrow micropores, V$_{DR}$(CO$_2$), for pores with mean pore sizes lower than 0.7 nm. Packing densities, ρ_{pack}, of the CNF-materials were measured in a mechanical press by applying a pressure of 739 N/mm^2 during 5 minutes. Additional high pressure H$_2$ adsorption measurements up to 20 MPa were performed at room temperature in an automated volumetric device [4].

Results and Discussion

In Table 1, the results for porosity characterization, the packing densities, as well as the activation yields of the investigated samples are listed. Interestingly, the unactivated CNF precursor already possesses some porosity, reaching an S$_{BET}$ of 520 m^2/g. All investigated activation methods are able to significantly increase the porosity. With physical activation by CO$_2$, the highest S$_{BET}$ of 2260 m^2/g is obtained. Furthermore, the CO$_2$ activated ACNFs reach high V$_{DR}$(CO$_2$) values, revealing a very narrow micropore size distribution. Fig. 1 compares the activation yield of physically activated CNFs (steam and CO$_2$) over the apparent S$_{BET}$. The slope of the CO$_2$ activation is much more favourable than for steam activation, rendering high surface areas with relatively high yields.

In Fig. 2, hydrogen adsorption isotherms at 77 K and sub-atmospheric pressures are shown for the CNF precursor, as well as ACNFs which were synthesized by chemical

Table 1. Porosity characterization of the initial CNF and the activated CNF materials.

Sample	S$_{BET}$ m^2/g	V$_{DR}$(N$_2$) cm^3/g	V$_{DR}$(CO$_2$) cm^3/g	ρ_{pack} g/cm^3	Yield wt.%
CNF	520	0.22	0.26	0.78	-
CNF-Na [1]	1515	0.60	0.41	-	17
CNF-K [1]	1765	0.68	0.45	0.74	30
CNF-S-1 [2]	1010	0.40	-	-	14
CNF-S-3 [2]	1760	0.72	-	-	7
CNF-S-5 [2]	2010	0.78	-	-	6
CNF-CD-12	1240	0.60	0.53	0.64	59
CNF-CD-24	1910	0.87	0.59	0.49	30
CNF-CD-32	2260	0.91	0.57	0.47	13
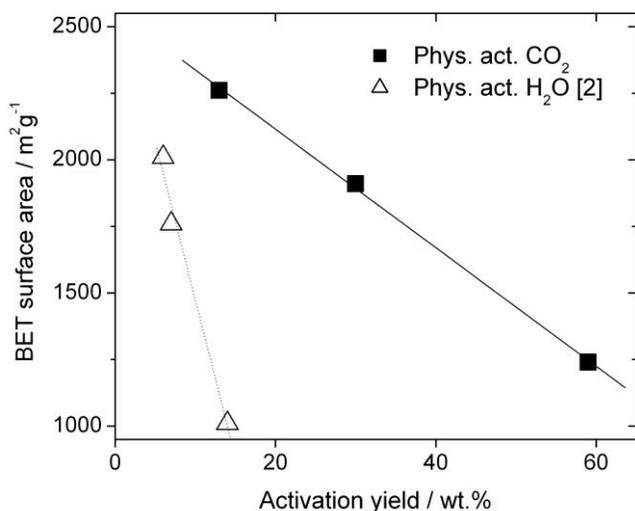
Fig. 1 Comparison of different methods for physical activation of polymer blend CNFs.

Fig. 2 Hydrogen adsorption isotherms at 77 K.

activation and by physical activation with CO_2. The unactivated precursor already adsorbs 1.26 wt.% under these conditions. The adsorption capacity is significantly increased after activation. Due to its narrow microporosity ($V_{DR}(CO_2)$ = 0.59 cm^3/g), the ACNF which was activated with CO_2 for 24 h reaches the highest adsorption amount (2.44 wt.%).

At low pressures and temperatures, the narrow microporosity plays a key role due to its high adsorption potential. However, at high pressures and temperatures, which are more interesting for vehicle hydrogen storage application, also other material properties become important. Under these conditions, a high packing density of the adsorbent is beneficial, in order to reach high total storage capacities. Apart from the adsorbed phase, the calculation of the total storage capacity also takes into account the compressed gas inside the void space of the material [1,4]. Thereby, the void space fraction can be estimated by V_{Void} = 1 - (ρ_{pack}/ρ_{skel}), whereby ρ_{skel} is the skeleton density of the material [1,4].

In Table 1 it can be seen that the investigated ACNFs reach high packing densities of up to 0.7 g/cm^3, making them interesting candidates for hydrogen storage application. At room temperature, sample CNF-CD-24 adsorbs over 1.2 wt.% (6 g/l) at 20 MPa. For the total storage capacity, this results in 17 g/l if a skeleton density of 2.22 g/cm^3 and a packing density of 0.49 g/cm^3 are taken into account. Such a high packing density, however, is only achieved by keeping the sample under pressure in the mechanical press. From an application point of view, it is desirable to retain the high density. This can be achieved by mechanical pressure or by preparing monoliths from the ACNFs. In the case of the monolith prepared from sample CNF-CD-24, the monolith density decreases only slightly in comparison with the original ACNFs to 0.46 g/cm^3.

Conclusions
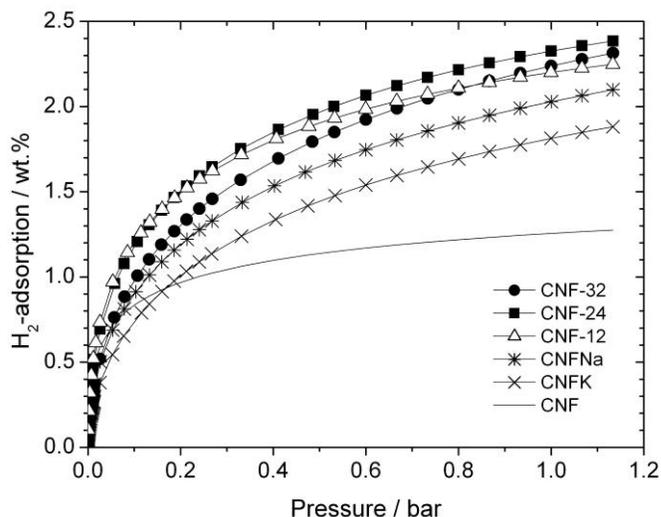
For the porosity development in polymer blend CNFs, physical activation with CO_2 is found to be advantageous in comparison with other activating methods. Thus, high specific surface areas are obtained with higher yields, and the porosity is significantly narrower. The latter causes an improved adsorption of H_2 under the investigated conditions. Furthermore, the synthesized ACNFs feature a high compressibility, which makes them a very promising candidate as hydrogen storage material. At room temperature and 20 MPa, total volumetric storage capacities of 17 g/l can be reached. The tendency to expand after compression can be avoided by monolith preparation from the ACNFs.

References
[1] Suárez-García F, Vilaplana-Ortego E, Kunowsky M, Kimura M, Oya A, Linares-Solano A. Activation of polymer blend carbon nanofibres by alkaline hydroxides and their hydrogen storage performances. Int J Hydrogen Energy 2009;34(22):9141-9150.
[2] Shiraishi S, Kurihara H, Ida Y, Oya A. Preparation of highly porous carbon nanofibers by polymer blend technique and its electric double layer capacitance, Extended Abstract, Carbon'03. In: An international conference on carbon. Oviedo (Spain): Spanish Carbon Group; 2003. p. 211–4.
[3] Lozano-Castelló D, Cazorla-Amorós D, Linares-Solano A, Quinn DF. Activated carbon monoliths for methane storage: influence of binder. Carbon 2002;40:2817–2825.
[4] Kunowsky M, Marco-Lozar, JP, Cazorla-Amorós, D, Linares-Solano A. Scale-up activation of carbon fibres for hydrogen storage. Int J Hydrogen Energy 2010;35(6):2393-2402.