Thesis Review. Synthesis of fibrous activated carbons and monoliths for hydrogen storage

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OBJECTIVES AND NOVELTY

For a future energy sector, hydrogen is considered a clean alternative to other fuels. As an ideal secondary energy carrier it can be produced from renewable energy sources (e.g., solar, wind, biomass, etc.), and converted very efficiently to electricity in fuel cells, emitting only water. However, one of the main obstacles which impedes the introduction of this technology is the absence of efficient storage solutions. This is strongly related to the low density of hydrogen, which exists as a supercritical fluid under normal conditions. In order to use hydrogen as a fuel, a number of different technologies are considered today. Among them, the high pressure storage in adsorbent materials is a promising technology. The adsorbents for such kind of application require very specific features, depending on the thermophysical storage conditions.

The overall research objective of this study was the synthesis and characterization of activated carbon fibers and nanofibers, as well as monoliths, in order to obtain suitable materials for hydrogen storage. The specific objectives of the research were:

- Identify the optimal parameters of activation, in order to synthesize activated carbon fibers (ACFs) with suitable hydrogen storage characteristics.
- Produce larger amounts of ACFs by up-scaling of the activation process.
- To study the synthesis of activated carbon nanofibers (ACNFs).
- To optimize the density of the ACFs and ACNFs by synthesizing monoliths from them.
- Measure the adsorption of H_2 on selected samples and evaluate their total storage capacities.
- Estimate the capacities of H_2 storage systems by taking into account the technical specifications of state-of-the-art H_2 storage vessels.

The main contribution of this work was the identification of the activation parameters for the synthesis of activated carbon fiber materials with tailored properties for hydrogen storage application. H_2 adsorption measurements on ACFs confirm and consolidate results previously reported in the literature. Despite this, exceptionally high hydrogen adsorption amounts were measured for an ACNF at 298 K and 20 MPa. The total H_2 storage capacity was established as a useful tool for material characterization. In addition, formulas have been developed for calculating the capacities of H_2 storage systems. These formulas provide the opportunity to evaluate the performance of tanks and adsorbents for H_2 storage *via* physisorption.

RESULTS

The research work presented in the Ph.D. Thesis deals with the synthesis of advanced activated carbon materials, in order to use them for hydrogen storage application. A total number of 90 samples were investigated, comprising activated carbon fibers (ACFs), activated carbon nanofibers (ACNFs), as well as activated carbon monoliths from different precursors.

Regarding the synthesis of activated carbon fibers (ACFs), it turned out that the carbonization temperature of the original carbon fiber had a high impact on the porosity development, a detail which previously had not been taken into account. Other activation parameters (activation time and temperature, nitrogen flow, mixing method, etc.) were also studied. By combining different carbonization temperatures of the precursors on the one hand and different amounts and types of activating agents on the other hand, samples with a wide range of porosity development were prepared. Thus, ACF samples with BET surface areas over 3000 m^2g^{-1} and very selective porosity distributions were synthesized. In particular, some samples revealed very narrow distributions of micropores and $V_{DR}(CO_2)$ values of around 0.8 cm^3g^{-1} which are particularly interesting for the storage of hydrogen at room temperature. In addition, two scale-up activations were successfully carried out, in order to synthesize large amounts of ACFs with suitable properties for hydrogen storage applications. The amount of sample produced was approximately an order of magnitude higher compared to the laboratory scale activations. The degree of activation was slightly higher for the scale-up activations. Therefore, higher porosity and lower yields than on laboratory scale were obtained. In both scale-ups, the produced ACFs reached BET surface areas of around 2300 m^2g^{-1}, high $V_{DR}(CO_2)$ up to 0.8 cm^3g^{-1} and packing densities around 0.6 g cm^{-3}.

Activated carbon nanofibers (ACNFs) were produced from a type of carbon nanofiber (CNF) of amorphous nature. Surprisingly, CO_2 was more effective when compared with other activating agents (H_2O, alkali hydroxides). When CO_2 was used as activating agent, a suitable porosity for storing H_2 was developed and better activation yields were obtained. BET surface areas up to 2000 m^2g^{-1}, $V_{DR}(CO_2)$ of 0.6 cm^3g^{-1} and packing densities near 0.5 g cm^{-3} were reached.

Monoliths were produced from activated carbons, ACFs, and ACNFs, reaching high densities up to 0.7 g cm^{-3}. These were higher than the bulk densities and the densities of the original compressed fibers and close to their packing densities. Furthermore, the porosity of the monoliths generally decreased in comparison with their precursors. The density increased with the amount of binder used for the monolith synthesis. In addition, a commercial high-density AC-monolith (ATMI Co.), which was produced from PVDC, was investigated, increasing its porosity by physical activation with CO_2.

Because of hydrogen's low heat of adsorption in comparison with other gases, its adsorption is favored at high pressures and/or at low temperatures. Both of the scenarios were investigated in the scope of the Thesis for selections of ACFs, ACNFs, and monoliths, covering a wide range of porosity. At liquid nitrogen temperature (77 K) and up to pressures of 4 MPa, hydrogen adsorption isotherms were measured in a gravimetric equipment. In Figures 1 and 2, the maximum H_2 adsorption amounts are plotted against the total volume of micropores, $V_{DR}(N_2)$, taking into account pore sizes < 2 nm. In Figure 1, the hydrogen adsorption amounts are expressed in gravimetric terms. Although different kinds of ACF and ACNF materials were measured, a linear tendency with $V_{DR}(N_2)$ can be observed, confirming results from the literature. In contrast, on a volumetric basis a linear correlation can only be adumbrated for small pore volumes (< 0.6 cm^3g^{-1}) and is clearly absent in the case of high pore volumes (see Figure 2). Here, the density of the adsorbent gains in importance. Thus, maximum amounts are obtained for optimum combinations of porosity and packing densities. The maximum H_2 excess adsorption values on gravimetric and volumetric basis at 77 K and 4 MPa were 5 wt.% and 30 g l^{-1}, respectively.

For measurements at room temperature (298 K) and high pressures up to 20 MPa, a volumetric device was used, and measurements of a significantly larger number of samples was performed, including ACFs, ACNFs, and different kinds of monoliths. In Figures 3 and 4, the maximum H_2 adsorption amounts obtained under these conditions are plotted against the volume of narrow micropores, $V_{DR}(CO_2)$, with pore sizes < 0.7 nm. On a gravimetric basis (see Figure 3), the values are more dispersed than the results obtained under cryogenic conditions (compare Figure 1); however, the results confirm that the narrow microporosity is the key porosity parameter which determines H_2 adsorption at room temperature, confirming previously reported results. Surprisingly, an exception was observed in the case of the ACNF materials: For these samples, the adsorption of H_2 was higher than expected from their porosities (see elevated tendency in Figure 3). This characteristic may be due to the presence of some very narrow microporosity in the CNFs. Such very narrow micropores may be accessible to H_2 at room temperature, but not to CO_2. The different kinetic molecular diameters of both gases (0.24 nm for H_2 *vs.* 0.33 nm for CO_2) could be the reason. This could also explain that at 77 K no exceptional high adsorption was measured for the CNF-based samples, because at such low temperature the kinetic adsorption energy of H_2 is much lower than at room temperature, so that both gases present similar accessibilities. The room temperature results on a volumetric basis are plotted in Figure 4. The values are even more dispersed that at 77 K (compare Figure 2), and no tendency can be found, due to the important impact of the adsorbents' densities. Interestingly, some "clusters" can be observed for different materials (see circles in Figure 4). For example, in the case of the ATMI-based monoliths, exceptionally high volumetric H_2 adsorption amounts were obtained. This can be contributed to their significant increase of narrow micropores upon activation, and their sustained high densities. In the case of the ACNFs, it can be observed that relatively low volumetric values are reached, due to their low densities. However, upon monolith synthesis, their densities can be substantially increased, so that significantly higher volumetric H_2 adsorption amounts are obtained (see arrows in Figure 4). The maximum excess adsorption values that were obtained at 298 K and 20 MPa were 1.3 wt.% and 7.5 g l^{-1}, respectively.

The total storage capacity is an extremely important parameter, because it accounts for the total number of gas molecules which is present in a given adsorption tank system. The molecules can either be adsorbed

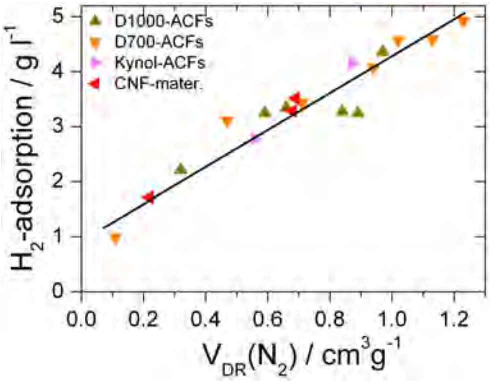

Figure 1. Maximum hydrogen adsorption amounts on a gravimetric basis, obtained at 77 K and up to 4 MPa, plotted against the total volume of micropores < 2 nm.

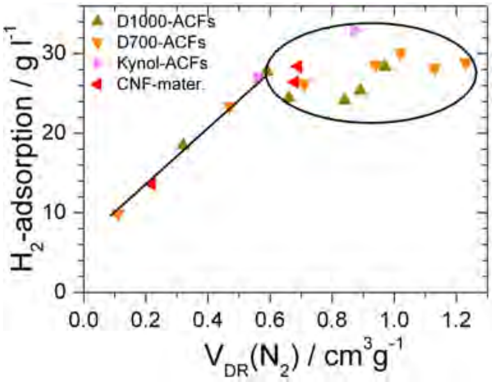

Figure 2. Maximum hydrogen adsorption amounts on a volumetric basis, obtained at 77 K and up to 4 MPa, plotted against the total volume of micropores < 2 nm.

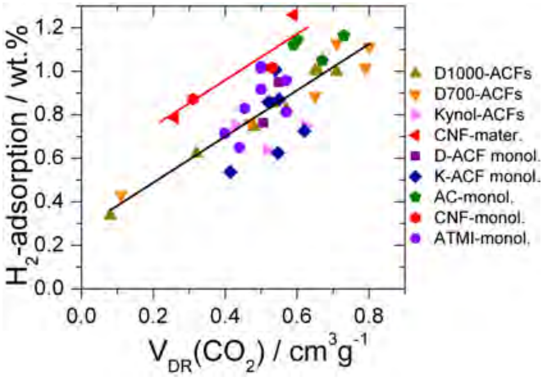

Figure 3. Maximum hydrogen adsorption amounts on a gravimetric basis, obtained at 298 K and up to 20 MPa, plotted against the volume of narrow micropores < 0.7 nm.

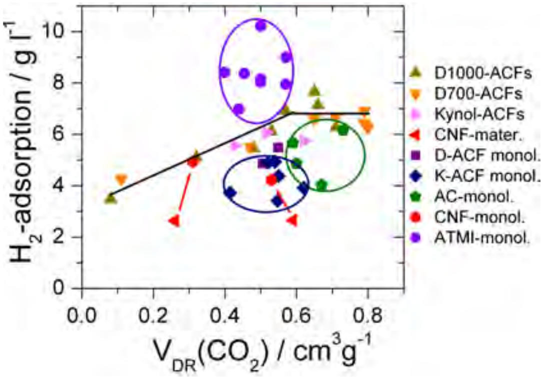

Figure 4. Maximum hydrogen adsorption amounts on a volumetric basis, obtained at 298 K and up to 20 MPa, plotted against the volume of narrow micropores < 0.7 nm.

in the porous structure of the adsorbent, or exist as a compressed gas phase in the void space (see schematic diagram in Figure 5). The latter contribution appears to be particularly important at high pressures and temperatures. The established formulas strongly depend on the appropriate selection of the material densities. For ACFs, a maximum value of 16.6 g l^{-1} was reached at 298 K and 20 MPa. The monolith synthesized from this sample reached a higher total H_2 storage capacity of 17.6 g l^{-1}. ACNFs also reached high values up to 17.4 g l^{-1}. At 77 K and 4 MPa, maximum values of around 39 g l^{-1} were reached.

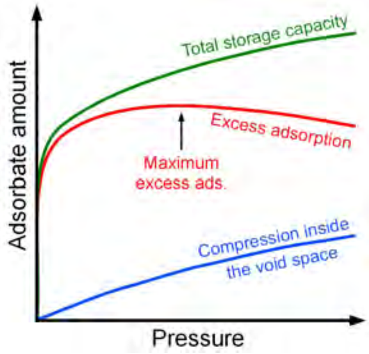

Figure 5. Schematic diagram of the adsorption isotherms, the compressed gas in the void space, as well as the total storage isotherm.

In order to calculate the capacity of whole H_2 storage systems, formulas were developed which can be applied to any adsorbate, considering various operating conditions and for different combinations of tanks and adsorptive properties. In addition, a dimensionless property κ was introduced which identifies if the storage capacity of an empty tank system can be increased by filling it with adsorbent material. Calculations for a number of existing H_2 containers were performed, assuming their filling with ACF samples that were synthesized in the scope of the Thesis. In all cases, the volumetric system storage capacities increased for storage tanks filled with adsorbent. The gravimetric system storage capacity also increased in the case of storage conditions of 77 K and 4 MPa. Only at 298 K and 20 MPa the gravimetric capacity of the empty vessel was higher compared to the tank filled with adsorbent.

CONCLUSIONS

The main contribution of this work was the identification of the activation parameters for the synthesis of activated carbon fiber materials with special properties for hydrogen storage. H_2 adsorption measurements on ACFs confirm and consolidate previously reported results in the literature. Despite this, exceptionally high amounts of hydrogen were adsorbed on ACNFs at 298 K and 20 MPa. The total H_2 storage capacity is found to being a useful tool for material characterization. In addition, formulas have been developed with the aim to calculate the storage capacities of whole H_2 storage systems. These formulas provide the opportunity to evaluate the performance of tanks and adsorbents for storing H_2 through physisorption.

Future research should focus on further characterization of fiber precursors that were carbonized at different temperatures, in order to optimize this activation parameter. In particular, the study of the influence of surface groups, which was not subject of this study, could be interesting. The scale-up of the activation process could be extended to furnaces with continuous feed; thus, substantially increasing the quantity of produced adsorbent. Similar to the activation process, also the washing step could be improved, *e.g.* through automatisation. The exceptionally high amount of H_2 adsorbed in ACNFs at room temperature and the provided hypothesis (high development of a very narrow porosity) should be further investigated. The total storage capacity of H_2 on a volumetric basis should be established as a standard characterization tool for H_2 storage in porous materials. In gravimetric terms, precise packing densities must be used, in order to avoid unrealistic and overestimated values. The proposed formulas to estimate the capacity of H_2 storage systems should be used, in order to evaluate and/or design tank systems specialized for the storage of gases by physisorption.

RELATED PUBLICATIONS

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