High-performances carbonaceous adsorbents for hydrogen storage

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Abstract. Activated carbons (ACs) with controlled microporosity have been prepared and their H₂ storage performances have been tested in a gravimetric device. Such adsorbents are natural Chinese anthracites chemically activated with alkaline hydroxides, NaOH or KOH. Outstanding total storage capacities of hydrogen, as high as 6.6wt.% equivalent to excess capacity of 6.2 wt.%, have been obtained at 4MPa for some of these adsorbents. These values of hydrogen adsorption are among the best, if not the highest, ever published so far in the open literature. They are well above those of some commercial materials, e.g. Maxsorb-3, considered as a reference of high-performance adsorbent for hydrogen adsorption. Such exceptional storage capacities may be ascribed to a higher volume of micropores (<2nm).

1. Introduction

Hydrogen is a renewable energy vector frequently proposed as an alternative to the current fossil fuel-based energy system to solve problems pertaining to energy distribution and environmental issues. However, the main drawback of hydrogen arises from its supercritical nature under standard conditions (Tc = 33.19K, Pc = 1.296MPa), giving it a very low density: only 90g m⁻³ at 1bar and 273K. The US Department of Energy set targets for hydrogen storage systems in light-duty vehicles in 2009. These targets correspond to a gravimetric capacity (i.e., the ratio between net useful energy and maximum system mass) of 4.5% or 1.5kWh kg⁻¹ (formerly: 6% or 2kWh kg⁻¹) in 2010, and of 5.5% or 3kWh kg⁻¹ (formerly: 9% or 3kWh kg⁻¹) in 2015 [1]. These new targets are still difficult to reach at room temperature. However, stationary applications are not limited by their weight and therefore technical solutions could be available in a shorter time.

The success of any future hydrogen economy depends on the development of inexpensive materials with sufficiently high hydrogen-storage capacity. Four alternatives for hydrogen storage can be anticipated: liquefaction, compression, physisorption, and storage in the form of metallic hydrides. Liquefaction and compression strategies have high operation costs. Moreover, compression needs high pressure operations, which causes high cost for both process and storage tank, and gives rise to safety issues related to high pressures Metal hydrides have incomplete reversibility and low charge/discharge kinetics. Porous and high-surface area activated carbons (ACs) are among the most important candidates to store efficiently hydrogen due to their low price, high surface area and tunable nanoporosity. Hydrogen storage by physisorption on activated carbons can be an interesting option in
stationary applications, wherein weight and volume are not limiting factors. Expected benefits are lower pressures thus safer operations, fast kinetics and complete reversibility.

Anthracites combine low cost, low ash content and an ideal microtexture for getting a tunable nanoporosity. In this study, we have prepared ACs from Chinese anthracite by varying systematically the activation temperature and the amount of activating agent (NaOH or KOH). We compared their performances to that of Maxsorb-3.

2. Experimental

We have prepared ACs by chemical activation, and the commercial AC Maxsorb-3 (formerly AX21) from Kansai Coke and Chemicals Co., Ltd. (Japan) was used for the sake of comparison. All the materials were characterized by N\textsubscript{2} and H\textsubscript{2} adsorption at 77K.

2.1. AC’s synthesis

The precursor of the ACs investigated here was Chinese anthracite from Taisi mine. It was first ground and sieved in order to collect the grains having an average size within the range 100 - 200\textmu m. The anthracite powder was then physically mixed with alkaline hydroxide (XOH): either sodium (X = Na) or potassium (X = K) hydroxide lentils (typical size 5 mm), according to various weight ratios XOH / anthracite, \( R \), ranging from 1.5 to 2.5. Additional ACs where synthesised by KOH activation with an \( R \) up to 5. The resultant mixture was introduced into a nickel crucible, and heat-treated in a horizontal furnace under a stream of nitrogen at constant heating rate of 5K min\textsuperscript{-1} up to the final activation temperature, \( T \). \( T \) was fixed within the range 973 – 1073K and maintained for 1h. The crucible was then allowed to cool down to room temperature under nitrogen flow. More details are given elsewhere [2, 3].

2.2. AC’s characterisation

2.2.1. N\textsubscript{2} adsorption. N\textsubscript{2} adsorption isotherms were obtained at 77K using an automatic adsorption apparatus, ASAP 2020 from Micromeritics. The samples were outgassed for 48h under vacuum at 523K prior to N\textsubscript{2} adsorption. Surface areas, \( S_{\text{BET}} \), were determined by the BET calculation method [4] applied to the adsorption branch of the isotherms. \( S_{\text{BET}} \) and pore volumes were estimated with a typical, maximum, uncertainty of 3\%. The pore-size distributions (PSD) were calculated by application of the DFT model [5] supplied by Micromeritics software, considering slit-shaped pores.

2.2.2. H\textsubscript{2} adsorption. Determination of H\textsubscript{2} storage properties at 77 K for the ACs was carried with a gravimetric device from VTI Corporation (Miami, USA) at ICB (Zaragoza, Spain). The system consists of a fully computer-controlled microbalance, which automatically measures the weight of the carbon sample as a function of time, with the same hydrogen pressure and sample temperature under control. Hydrogen isotherms were obtained by setting pressure steps within the range 0 - 8MPa at 77K. For each run, approximately 500mg of activated carbon sample were placed into a bucket made from stainless steel mesh. Hydrogen pressure was gradually increased to prevent disruption of the microbalance, until the desired value was reached. A pressure transducer (accuracy 0.05\% of the full pressure range up to 10MPa) was used to monitor hydrogen pressure in the system. More details have been given elsewhere [2, 3]. Repeatability was always found to be very satisfactory, leading to relative errors lower than 3\% on each measurement.

3. Results and discussion

3.1. Effect of \( R \) and \( T \)

Figure 1 and Figure 2 show the effect of \( R \) and \( T \), respectively, on H\textsubscript{2} storage capacity. Absolute (total) H\textsubscript{2} storage capacities are shown. The increase of \( R \) and \( T \) produced a nearly linear increase of H\textsubscript{2} storage for both activating agents. The slope of the fitted straight line of the H\textsubscript{2} storage capacity with \( T \) was higher for KOH than for NaOH.
Figure 1. Evolution of H\textsubscript{2} storage capacity with the activation ratio, \(R\) (▲ NaOH, ■ KOH).

H\textsubscript{2} storage capacity increased with both \(R\) and \(T\), and was always higher on ACs produced by KOH activation. The use of KOH allowed obtaining \(S_{BET}\) values ranging from 1688 to 2772 m\textsuperscript{2} g\textsuperscript{-1}, whereas NaOH led to lower surface areas, within the range 1500 – 2065 m\textsuperscript{2} g\textsuperscript{-1}.

Figure 2. Evolution of H\textsubscript{2} storage capacity with the activation temperature, \(T\) (▲ NaOH, ■ KOH).

Figure 3 shows the evolution of the pore-size distribution of three ACs prepared with KOH when \(T\) increased from 1023 to 1073K, at \(R=2\), and when \(R\) increased from 2 to 2.5, at \(T=1023K\). Increasing \(R\) and \(T\) increased the micropore volume but also the fraction of wider micropores (0.7-2 nm) and that of mesopores (> 2 nm).

Figure 3. PSDs of three ACs prepared by KOH activation (▲ \(T=1023K\) and \(R=2\), ■ \(T=1073K\) and \(R=2\) and ◆ \(T=1023K\) and \(R=2.5\)).

In other words, the development of surface area by KOH activation is always accompanied of pore widening. Therefore, PSDs shifted to wider pores can lead to samples exhibiting higher H\textsubscript{2} adsorption capacities, provided that a high volume of micropores (< 2 nm) still exists.

3.2. Further H\textsubscript{2} storage improvements on KOH-ACs

Based on the previous experiments, we decided to continue our study using only KOH as activating agent and increasing \(R\) up to 5. We got ACs with \(S_{BET}\) as high as 3434 m\textsuperscript{2} g\textsuperscript{-1}. These \(S_{BET}\) are considered as apparent surface areas, given that it is not physically possible to have carbon materials with a surface higher than 2630 m\textsuperscript{2} g\textsuperscript{-1}. 
Figure 4 shows the total hydrogen storage capacity of all the ACs prepared by KOH activation. Total hydrogen storage capacity as high as 6.6 wt.%, equivalent to 6.2 wt.% excess capacity, were obtained. The US DOE target for 2010 was 5.5 wt.% for hydrogen storage systems (AC + tank). However, the performances reached in this study are among the best reported by the latest reviews [6, 7] and recent literature in general, e.g. [8-10]. Therefore, our materials are among the best reported in the literature so far.

Figure 4. Total $H_2$ storage capacity (wt. %) as a function of $S_{BET}$.

We have already shown [2] that a linear relationship is observed between maximum hydrogen uptake at 77K and BET surface area only if the latter is not higher than typically 2630 m$^2$/g. Above such a value, a plateau is reached due to a saturation of $H_2$ storage capacity at 2630 m$^2$/g, and a slight decrease was found for the highest surface areas probably due to the broadening of the pores.

3.3. Comparison with Maxsorb-3
Maxsorb-3 has been claimed to adsorb about 6 wt. % of hydrogen at 77K and 5MPa, 5 wt. % being already reached at 2MPa [11]. Other results on the same material are about 3 wt. % at 80K and 10MPa [12] and, at room temperature: 1 wt. % at 5MPa [13], and 1.6 wt. % at 70MPa [12].

Figure 5. Total $H_2$ storage (wt. %) isotherms at 77K for Mawsorb-3 and for our best lab-made AC. Adsorption (full symbols) - desorption (open symbols).
Figure 5 shows the H$_2$ adsorption isotherm for the best of our ACs and Maxsorb-3. Our lab-made AC reached 6.6 wt. % whereas Maxsorb-3 reached “only” 5.8 wt. %. H$_2$ adsorption was totally reversible and desorption was fast. Our lab-made AC has a higher $S_{BET}$ than Maxsorb-3: 3310 and 3203 m$^2$ g$^{-1}$, respectively. However, this small difference in the $S_{BET}$ can not justify such a difference of H$_2$ storage capacity. The reason of the higher performances of our lab-made AC is based on its PSD shifted towards narrower pores. Our lab-made AC indeed presents a higher faction of micropores (<2nm) calculated by the DFT method.

4. Conclusions
We have prepared highly microporous ACs by activation with NaOH or KOH, which showed outstanding performances for hydrogen storage at 77K. The ACs with the highest H$_2$ storage performances were obtained by KOH activation, using an activating agent to precursor weight ratio of 4 or higher, and activation temperatures higher than 1023K. Some of these ACs reached a total hydrogen storage capacity of 6.6 wt.%. These performances are well above those of the well-known commercial AC Maxsorb-3. Such exceptional hydrogen storage capacities may be ascribed to a higher volume of micropores (<2nm) of our ACs when compared to Maxsorb-3.

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References
[1] http://www1.eere.energy.gov/hydrogenandfuelcells/storage/pdfs/targets_onboard_hydro_storag e_explanation.pdf (consulted 23/03/2011)
[2] Fierro V, Szczurek A, Zlotea C, Marêché JF, Izquierdo MT, Albiani A, Latroche M, Furdin G and Celzard A 2010 Carbon 48 1902
[3] Fierro V, Zhao W, Izquierdo MT, Aylon E and Celzard A 2010 Int. J. Hydrogen Energ. 35 9038
[4] Brunauer S, Emmet PH and Teller E 1938 J. Am. Chem. Soc. 60 309
[5] Tarazona P 1995 Surf. Sci. 331-333 989
[6] Yürüm Y, Taralp A and Veziroglu TN 2009 Int. J. Hydrogen Energ. 34 3784
[7] Zubizarreta L, Arenillas A and Pis JJ 2009 Int. J. Hydrogen Energ. 34 4575
[8] Wu HC, Li YY and Sakoda A 2010 Int. J. Hydrogen Energ. 35 4123
[9] Huang CC, Chen HM and Chen CH 2010 Int. J. Hydrogen Energ. 35 2777
[10] Suarez-Garcia F, Vilaplana-Ortego E, Kunowsky M, Kimura M, Oya A and Linares-Solano A 2009 Int. J. Hydrogen Energ. 34 9141
[11] Chahine R and Bose TK. 1994 Int. J. Hydrogen Energ. 19 161.
[12] de la Casa-Lillo MA, Lamari-Darkrim F, Cazorla-Amoros D and Linares-Solano A 2002 J. Phys. Chem. B 106 10930
[13] Ye Y, Ahn CC, Witham B, Fultz B, Liu J, Rinzler AG, Colbert D, Smith KA, Smalley RE 1999 Appl. Phys. Lett. 74 2307