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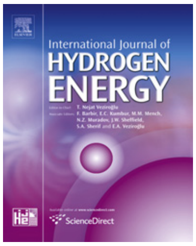

Optimization of activated carbons for hydrogen storage

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ABSTRACT

Activated carbons (ACs) having hydrogen storage performances among the highest reported so far (i.e. 6.6 wt. % at 77 K and 4 MPa) are presented. These materials were prepared by chemical activation of anthracite with KOH. The effects of two experimental parameters: KOH/anthracite weight ratio (W) and activation temperature (T), on the hydrogen storage capacity were studied by application of central composite design and response surface methodology. A quadratic model was developed for correlating W and T to the hydrogen storage capacity. The analysis of variance showed that W the only significant parameter in the range of the experimental conditions tested. Our optimized AC showed higher hydrogen capacity in terms of absolute and excess storage properties than the well-known MAXSORB-3.

1. Introduction

Hydrogen holds the potential to provide a clean, safe and affordable energy carrier for automotive and stationary applications. The targets for hydrogen storage systems in light-duty vehicles given by the US Department of Energy correspond to gravimetric capacities of 4.5% in 2010 and 5.5% in 2015 [1]. These targets are difficult to reach at room temperature. However, stationary applications are not limited by their weight and therefore technical solutions might be available at shorter time.

In activated carbons (AC), hydrogen significantly gets denser due to the high surface area and to the number of narrow pores available for its adsorption [2,3]. In a previous study [4], we showed that surface area and micropore volume of activated carbons prepared by chemical activation of anthracite with KOH increased linearly with activation temperature (T) and KOH/anthracite weight ratio (W) within the ranges 973–1073 K and 1.5–2.5, respectively. Hydrogen storage increased linearly with the surface area as far as the latter didn't exceed its theoretical limiting (geometrical) value of 2630 m^2/g [5]. Based on the results reported by various authors [3,6–8] and including our own data [5], we demonstrated that the correlation between S_{BET} and H_2 storage capacity at 77 K was always improved when fitting a straight line to the data points corresponding to materials of surface area lower than 2630 $m^2\ g^{-1}$. The best adsorbents were obtained using KOH as activating agent. Taking into account that the pore texture can not be infinitely developed, we predicted that optimal activation conditions should exist for

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obtaining the highest possible hydrogen storage capacity. We have also experimentally shown that a maximum in hydrogen adsorption on activated carbons exists [9], and this maximum is very close to the one calculated by Schlapbach and Züttel [5]. Finally, we demonstrated that Taisi anthracite used as AC precursor leads to a more favourable pore size distribution (PSD) for hydrogen storage than does the famous MAXSORB-3. The PSD of Taisi was indeed shifted towards narrower pores for similar surface areas [10]. In the same study, we obtained apparent surface areas higher than 3000 m^2/g for values of W higher than 3.

Response surface methodology (RSM) is a useful optimization tool, and is also used to study the interactions of two or more variables. RSM has been used to optimize ACs production [11,12], in order to get maximum dyes adsorption [13–15] or to study the variation of their physicochemical characteristics as a function of the activation conditions [16]. As far as we know, RSM has never been applied to optimize ACs for hydrogen storage.

The present manuscript is focused on the optimization of ACs for hydrogen storage by studying the effect of activation condition parameters W and T, using KOH as activating agent. We used central composite design (CCD) for planning experiments and RSM for studying the interaction between the activation conditions.

2. Experimental

2.1. Preparation of the activated carbons

The precursor of the ACs investigated here was Chinese anthracite from Taisi mine, with an average particle size within the range 100–200 μm. The anthracite powder was physically mixed with potassium hydroxide (KOH), according to various KOH/anthracite weight ratios (W). 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 (3K min^{-1}) up to the final activation temperature (T) which was maintained for 2 h. The crucible was then allowed to cool down to room temperature under nitrogen flow [4,9].

2.2. Experiment design and statistical analysis

Central Composite Design (CCD) is the most popular experiment design to apply RSM. It has three groups of design points: (a) two-level factorial or fractional factorial design points; (b) axial points (sometimes called "star" points); (c) center points. In this study, two parameters were varied: KOH/anthracite weight ratio (W) and activation temperature (T). The central point was set to $T = 1023$ K and $W = 3$.

Table 1 shows the scheme and complete design matrix of the experiments carried out. There are four factorial points and four star points, and the central point was repeated 3 times in order to get a good estimate of experimental (or pure) error. The location of the star points in the CDD was fixed at $\sqrt{2}$. The complete design matrix comprised 11 ACs. Design Expert software version 7.0 (STAT-EASE Inc., Minneapolis, USA) was used for regression analysis of the experimental data, fitting equations and evaluating their statistical significance.

Table 1 – Scheme and central composite design matrix used ($\alpha = \sqrt{2}$).

# AC	Factors_coded		Factors_Actual	
	T	W	T (K)	W
1	0	$\sqrt{2}$	1023	4.4
2	0	$\sqrt{2}$	1023	1.6
3	$-\sqrt{2}$	0	988	3.0
4	−1	1	998	4.0
5	0	0	1023	3.0
6	0	0	1023	3.0
7	$\sqrt{2}$	0	1058	3.0
8	1	−1	1048	2.0
9	1	1	1048	4.0
10	0	0	1023	3.0
11	−1	−1	998	2.0

2.3. Structural characterization of the ACs

N_2 adsorption-desorption isotherms were obtained at 77 K using a Micromeritics ASAP 2020 automatic apparatus. The samples were degassed for 48 h under vacuum at 523 K prior to any adsorption experiment. CO_2 adsorption was not used for characterizing the materials prepared in this study due to the full accessibility of the pores to N_2 at 77 K. Indeed, porosity was well developed and no diffusion limitation for N_2 was observed.

N_2 adsorption data were obtained and treated as described elsewhere [4,9] for obtaining: (i) surface area, S_{BET}, from the BET calculation method [17]; (ii) micropore volume, V_{DR}, according to the Dubinin-Radushkevich (DR) method [18] and refs. therein; (iii) total pore volume, $V_{0.99}$, defined as the volume of liquid nitrogen corresponding to the amount adsorbed at a relative pressure $P/P_0 = 0.99$ [19]; mesopore volume, V_{me}, calculated as the difference $V_{0.99}$ - V_{DR}. The average micropore diameter, L_0 [20], and the pore size distributions by application of the Density Functional Theory (DFT) [21] were also calculated.

2.4. Measurement of hydrogen storage capacities at 77 K

Determination of absolute hydrogen uptake at 77 K was carried at Instituto de Carboquimica (Zaragoza, Spain). The apparatus was a gravimetric analyser from VTI Corporation (Miami, USA). Hydrogen isotherms were obtained by setting pressure steps within the range 0–8 MPa at 77 K. Determination of excess hydrogen storage at 77K and up to 8 MPa was carried out with a volumetric device equipped with calibrated and thermalised volumes and pressure gauges at Institut de Chimie et des Matériaux Paris-Est (Thiais, France). More details are given elsewhere [4,9].

3. Results and discussion

3.1. AC characterization

Table 2 shows the textural characterization determined by N_2 adsorption at 77 K and absolute hydrogen storage for all the ACs prepared. S_{BET} varied from 1673 to 3451 m^2/g, V_{DR} from 0.64 to 1.05 cm^3/g, and $V_{0.99}$ from 0.75 to 1.39 cm^3/g. ACs were