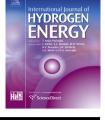Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

CrossMark

Hydrogen storage in activated carbons produced from coals of different ranks: Effect of oxygen content

M.C. Tellez-Juárez [a,b,c], V. Fierro [a,*], W. Zhao [a,c,d], N. Fernández-Huerta [e], M.T. Izquierdo [e], E. Reguera [b], A. Celzard [a,c]

[a] Institut Jean Lamour, UMR CNRS 7198, ENSTIB, 27 rue Philippe Séguin, CS 60036, 88026 Epinal cedex, France
[b] Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada del Instituto Politécnico Nacional, Unidad Legaria, Legaria 694, Col. Irrigación, México, D. F., Mexico
[c] Université de Lorraine, ENSTIB, 27 rue Philippe Séguin, CS 60036, 88026 Epinal cedex, France
[d] College of Material Engineering, Fujian Agriculture & Forestry University, Fuzhou, Fujian 350002, China
[e] Instituto de Carboquímica (ICB-CSIC), Miguel Luesma Castán, 4, 50018 Zaragoza, Spain

ARTICLE INFO

ABSTRACT

20 activated carbons (ACs) were prepared by activation of four coals of different ranks (bituminous, low-ash bituminous and sub-bituminous coals, and one anthracite) with potassium hydroxide, in order to evaluate their hydrogen storage capacities at −196 °C. The effect of surface area and oxygen content on hydrogen storage was examined. Oxygen content was determined by temperature-programmed desorption. The significance of oxygen content on hydrogen storage capacity was evaluated by Analysis of Variance (ANOVA). Apparent surface areas higher than 3000 m^2 g^{-1} and hydrogen adsorption as high as 6.8 wt.% were obtained. The best results were obtained with ACs from bituminous coals. No significant effect of oxygen content on hydrogen adsorption was observed. We concluded that surface area controls hydrogen storage capacity at −196 °C.

1. Introduction

The development of a viable hydrogen storage system is one of the key challenges which must be solved prior to the establishment of a hydrogen economy. One of the envisaged options to store hydrogen is adsorption on high surface area-porous materials such as activated carbons (ACs) [1,2]. Thus, ACs with very high surface areas have been prepared, and hydrogen adsorption capacities as high as 6.6 wt.% have indeed been determined at −196 °C [3–5]. The drawback of adsorption on ACs is the requirement of using low temperatures, because the typical heat of adsorption (ΔH_{ads}) of hydrogen on carbon is roughly 6 kJ mol^{-1} [6]. This value is well below the 20–30 kJ mol^{-1} fixed by the US Department of Energy (DOE) as a goal for hydrogen storage systems to be used for automotive applications. However, hydrogen adsorption capacities are not only governed by the porous texture of activated carbons (ACs) but also by their surface chemistry [7–10]. Indeed, a possible strategy for increasing the strength

---

of the gas–solid interaction, and hence the hydrogen storage capacity of ACs, is the introduction of metal nanoparticles [11–14] or heteroatoms in the carbon matrix [15–18].

Oxygen is by far the most conventional heteroelement present on carbon surface. It is spontaneously present, even at room temperature, and forms different types of organic functionalities, regardless of the nature of the carbon. Oxygen groups modify the polarity of carbon surface and therefore might affect its interaction with hydrogen molecules. Published theoretical and experimental studies concerning the effect of oxygen functional groups on hydrogen storage capacities are contradictory. Schimmel et al. [19] evaluated hydrogen storage in different carbon structures and concluded that hydrogen uptake is controlled by the number of accessible aromatic C–C bonds in the sample, which is related to the surface area. Agarwal et al. [20] reported that hydrogen storage capacity increased with the amount of acidic groups present on carbon surface. Bleda-Martínez et al. [21] studied the importance of dangling carbon bonds in hydrogen adsorption, and concluded that unsaturated oxygen sites were responsible of high hydrogen uptakes. Llorens and Pera-Titus [22] reported that surface heterogeneity is almost unchanged after oxidation and predicted by a model that the introduction of polar molecules does not affect the hydrogen-carbon adsorption interaction. Huang et al. [23] evaluated the textural characteristics of ACs before and after an oxidation process, and found that hydrogen capacity was lowered when the amount of oxygen-containing functional groups increased. Zhao et al. [24] showed that the presence of functional groups has a negative effect on hydrogen adsorption on activated carbons due to repulsive interactions between hydrogen molecules and functional groups. Georgakis et al. [25] suggested a molecular model for hydrogen adsorption in microporous carbonaceous materials, and concluded that functional groups induce steric hindrances and decrease the available space for hydrogen molecules. Moreover, functional groups increase the material density, therefore somewhat decrease the adsorbed amount per unit mass. Takagi et al. [26] evaluated the hydrogen adsorption capacity in activated carbon fibres and stated that the hydrogen uptake depends on micropore width, which can be blocked by oxygen-containing functional groups.

Therefore, the effect of oxygen content on hydrogen storage capacity is still debated and, most times, it is difficult to separate the combined effects of surface area and surface chemistry. In the present study, we examined the effect of oxygen content on hydrogen storage capacity based on 20 ACs produced by potassium hydroxide activation of four different rank coals. The effect of surface area was also taken into account. Oxygen content was determined by temperature-programmed desorption. The significance of oxygen content was evaluated by Analysis of Variance (ANOVA).

2. Experimental

2.1. Materials synthesis

ACs were produced by chemical activation with potassium hydroxide (KOH) of four Mexican raw coals, having different ranks: anthracite (A), bituminous (B), low-ash bituminous (LaB) and sub-bituminous (SB) coals. These coals were ground until an average particle size within the range 100–200 μm was obtained. We studied the effect of coal rank, activation temperature (T) and KOH/coal weight ratio (W) on apparent surface area and hydrogen storage capacity. More details about AC preparation were given elsewhere [3–5]. For each coal, we prepared ACs by fixing $W = 4$ at different activation temperatures of 700, 750 or 800 °C, or by fixing $T = 750$ °C at different values of W of 3, 4 or 5. Therefore, 20 different ACs were thus prepared and investigated.

2.2. Physicochemical characterisation

Proximate analysis of samples was carried out according to ISO-589-1981, ISO-1171-1976 and ISO-562-1974 standards for moisture, ash and volatile matter contents, respectively.

ACs textural characterisations were carried out by physical adsorption of N_2 at −196 °C, using a Micromeritics ASAP 2020 automatic adsorption apparatus. The samples were degassed for 48 h under vacuum at 250 °C prior to any adsorption experiment. Nitrogen adsorption data were obtained and treated as described elsewhere [3–5], and references therein] for obtaining: (i) surface area from the BET calculation method, S_{BET}; (ii) micropore volume, V_{DR}, according to the Dubinin-Radushkevich (DR) method.

Temperature-Programmed Desorption (TPD) runs were carried out with a homemade instrument, consisting of a tubular quartz reactor placed inside an electrical furnace and an on-line analysis of the evolved gases by mass spectrometry. In a typical TPD experiment, the sample was heated up to 1100 °C in a high-purity argon flow at a heating rate of 10 °C min^{-1}. The amounts of CO and CO_2 evolved at each temperature were measured continuously with a Pfeiffer quadrupole mass spectrometer. The calibrations for CO and CO_2 were carried out by standards diluted in Ar. In a typical run, 0.3 g of AC was placed in a horizontal quartz tubular reactor under an Ar stream of 30 mL min^{-1}.

Determination of hydrogen adsorption ($H_{2\ ads}$) isotherms at −196 °C within the range 0–8 MPa was carried with a gravimetric device analyzer (VTI Corporation). Details of experimental set-ups and measurement procedures have been given elsewhere [3–5]. The corresponding excess hydrogen ($H_{2\ exc}$) isotherms were measured with a volumetric device (HPVA-II, Micromeritics). Before each measurement, the samples were outgassed overnight under primary vacuum at 250 °C. The sample holder was immersed in liquid nitrogen and high-purity hydrogen was introduced step by step up to 8 MPa. All measurements were done twice to verify the repeatability. The error was lower than 0.1 wt.%.

3. Results and discussion

3.1. Coal characterisation

Table 1 shows the proximate analyses in dry basis of the four coals used as ACs precursors. Fixed carbon content decreased in the order A (86.30%) > LaB (63.11%) > B (47.92%) > SB (33.25%). The opposite trend was observed for ash content, so