



Short communication

Heat of adsorption and binding affinity for hydrogen on pitch-based activated carbons

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ABSTRACT

The distribution of the binding site affinity and isosteric heat of adsorption of hydrogen at (i) 77 K and 100 kPa and (ii) 298 K and 10 MPa on five pitch-based activated carbons, four of which contain different heteroatoms (Si, B, Ti or Fe) were studied using a Sips isotherm and the Clausius–Clapeyron expression, respectively. Based on the studies with the Sips isotherm, the hydrogen was adsorbed at 77 K on binding sites of pitch based activated carbons having different binding affinity (heterogeneous), whereas at 298 K the hydrogen was deposited only on a single class of binding sites (homogeneous). The binding site affinity of the activated carbons at 77 K was unimodally distributed, exhibiting a quasi-Gaussian shape at the studied experimental conditions (100 kPa). The binding affinity of activated carbons for hydrogen at both 77 and 298 K was found to be linearly proportional to the total volume of micropores (V_{N_2}) and the volume of narrow micropores (V_{CO_2}). The isosteric heat of the activated carbons was obtained by applying the Sips isotherm in the Clausius–Clapeyron equation and was found to be 3.05–6.9 kJ/mol. The values calculated suggest that the addition of heteroatoms to activated carbons has a minor effect on the isosteric heat at the experimental conditions used.

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1. Introduction

Hydrogen energy is considered to be an alternative for fossil fuels as it is clean and can be easily produced; additionally, it has a “lower heating value” (LHV) of 51532 Btu/lb and a “higher heating value” (HHV) of 61002 Btu/lb and water is the only clean oxidation product. The storage of hydrogen is a key issue especially in on-board hydrogen storage when used in hydrogen based fuel cells [1]. Reversible adsorption of hydrogen on carbonaceous materials has been attracting much interest, as it can be realized from the pioneering works reporting the hydrogen adsorption behavior of carbon nanotubes, graphite fibres, activated carbon, etc. [2–8]. Previous studies by several researchers show that the storage capacity of these materials is greatly influenced by the surface area, pore volume and pore size distribution [4,9,10]. Chu et al. [11] reported a linear dependence between surface area and the hydrogen storage capacity of adsorbent materials. The same authors found that the storage capacity of the adsorbent increases with pore size, reaching a maximum followed by a decrease in hydrogen storage capacity. To enhance the low hydrogen uptake at room temperature by physical adsorption several treatment methods, including the deposition of metallic compounds onto the activated carbon surface, have been

proposed [4,6–8]. Yang and Wang [12] showed that the doping of activated carbon with a metal ion, ruthenium, enhanced the hydrogen storage capacity by a factor of two when compared to that of undoped carbon. Likewise, Gallego et al. [13] showed that the palladium doped nanoporous carbons adsorb more hydrogen than that of corresponding carbon fiber without metal ions.

In our earlier works we found that pitch-based activated carbons containing heteroatoms could be useful materials for the storage of hydrogen gas at supercritical conditions [4]. The intentionally added chemical compounds to the precursor altered the structure of the pitch and the adsorptive properties of the resulting activated carbons; this could be due to the modification of the reactions taking place along pyrolysis. It was observed in our earlier work [4] that: i) the incorporation of heteroatoms somewhat altered the storage capacity of the activated carbons and ii) that the hydrogen uptake decreased with increasing temperature, as expected; however, the extent of the decrease in hydrogen uptake capacity with temperature was found to be different for each adsorbent. These differences in hydrogen uptake at different temperature are usually governed by the heat of adsorption [14] and the differences in performance of these adsorbents at different experimental conditions could be due to the differences in access of hydrogen molecules to the binding sites on the surface of these adsorbents. Thus, the estimation of the binding site affinity distribution and the isosteric heat of adsorption are important in order to learn about the practical utility of these materials for hydrogen storage purposes. In order

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to theoretically estimate the binding affinity distribution and the isosteric heat of adsorption of hydrogen, an attempt is made here to estimate these parameters using Sips isotherm. The performance of the pitch-based activated carbons as hydrogen storage materials is compared with some established materials based on the concepts of isosteric heat of adsorption. In addition, to our knowledge it is the first time that the mean binding affinity coefficient of different activated carbons with different physico-chemical properties is estimated and correlated to the structure of these materials.

2. Experimental

2.1. Pitch-based activated carbons

An aromatic petroleum residue (ethylene tar-R1) [15,16] was mixed, individually, with four different compounds, triphenylsilane (TPS), pyridine borane complex (PyB), tetrabutyl orthotitanate (TBO) and ferrocene (FC) in an ultrasonic bath for an hour, to give mixtures containing 2 wt.% of Si, Fe and Ti or 1 wt.% of B. All compounds are found to be apparently soluble in the petroleum residue. Pyrolysis of the mixtures was performed at 440 °C, soak time of 4 h and 1 MPa pressure, thus leading to pitches which contain the heteroatom: PSi, PB, PTi and PFe. A reference pitch P was also prepared. The activated carbons (PA, PSiA, PBA, PTiA and PFeA) were prepared from the respective petroleum pitches as follows: KOH and the pitch were mixed in a ball mill during 30 min with a impregnation ratio of KOH/carbon of 3/1 (this ratio is obtained by mixing 75% KOH and 25% carbon by weight) and then thermally treated in a horizontal furnace at 800 °C under nitrogen flow of 100 ml/min, soak time of 2 h. Finally, the activated carbon was washed in a Soxhlet apparatus for 24 h with water and dried at 110 °C for 24 h in a vacuum oven.

2.2. Adsorption experiments

The hydrogen adsorption isotherms for the undoped and doped pitch-based carbons were obtained using a homemade automatic volumetric equipment described elsewhere [4], which features two pressure transducers covering the pressure range up to 0.1 MPa and 10 MPa, respectively. A liquid nitrogen constant temperature bath and a thermostatic bath was used for performing the adsorption experiments at 77 K and 298 K, respectively. The samples were degassed at 1×10^{-4} Pa and 250 °C prior to the adsorption experiments.

The porosity of the activated carbons was deduced from the adsorption isotherms of N₂ at 77 K and CO₂ at 298 K using a homemade automatic volumetric equipment. The total volume of micropores, size lower than 2 nm (V_{N_2}) was determined by the application of Dubinin–Radushkevich equation to N₂ adsorption isotherm. The volume of mesopores (V_{meso}) was estimated from the difference between the amount of N₂ adsorbed at $P/P_0 = 0.95$ and the total micropore volume (V_{N_2}). The volume of narrow micropores, size lower than 0.7 nm, (V_{CO_2}) was also determined by the application of Dubinin–Radushkevich isotherm to CO₂ adsorption isotherm. The detailed characterization results of the studied activated carbons are discussed elsewhere [4].

3. Theory

3.1. Adsorption isotherm

The Sips [17,18] isotherm used in this study was originally proposed to explain the distribution of the adsorption energy of the sites of a solid surface when the adsorption isotherms are known. Sips isotherm reduces to the Freundlich type for low pressures,

but exhibits saturations for high pressures. The simplest expression which was presented by Sips in the actual form of Freundlich isotherm is given by

$$n = \frac{n_{\max} K_s P^{m_s}}{1 + K_s P^{m_s}} \quad (1)$$

where n_{\max} is the maximum adsorption capacity of the activated carbon for hydrogen, K_s is the Sips isotherm constant and m_s is the Sips isotherm exponent, which should fall within the range from -1 to $+1$. During non-linear optimization the initial values for n_{\max} and K_s were obtained from the Langmuir isotherm and the m_s values were fixed between the range -1 to $+1$ while running an iteration procedure using the solver add-in, Microsoft Spreadsheet, Microsoft Excel, Microsoft Corporation.

3.2. Binding site energy distribution

Assuming the gas is adsorbed on the surface in a molecular state without dissociation and that $N(K)$ is the number of active centers whose energy of adsorption per mole lies between K and dK , then the affinity distribution can be obtained from the solution to a Langmuir adsorption integral [19]

$$N = \int_{-\infty}^{\infty} \frac{N(K)PK}{1 + PK} d(\log K) \quad (2)$$

Solution to Eq. (2) gives the corresponding affinity distribution function $N(K)$, which provides the number of sites (N) with respect to the association constant (K).

Eq. (2) is an ill-posed problem and it has no general analytical solution, even if $N(K)$ is assumed to have a perfect form [19]. Several attempts have been made in the literature to find a solution to Eq. (2) considering the importance of this expression. Recently, Umpleby et al. [19] presented an analytical solution combining the numerical approximation of Huston [20] and Sips isotherm

$$N(i) = n_{\max} \left(\frac{1}{K(i)} \right)^{m_s} \left(1 + 2K_s \left(\frac{1}{K(i)} \right)^{m_s} \right) + \left(\frac{4K_s(1/K(i))^{m_s} m_s^2 - K_s^2(1/K(i))^{2m_s} m_s^2 - m_s^2}{(1 + K_s(1/K(i))^{m_s})^4} \right) \quad (3)$$

Eq. (3) is a general function for the affinity distribution according to the Sips isotherm, which enables to calculate the number of binding sites $N(i)$ having association constant $K(i)$ using the Sips isotherm parameters, n_{\max} , K_s and m_s .

3.3. Isosteric heat of adsorption

The isosteric heat of adsorption of hydrogen on the different activation carbons studied is calculated from the isosteres using the Clausius–Clapeyron equation given by

$$-\frac{Q_{st}}{R} = \left[\frac{d \ln p}{d(1/T)} \right]_{\theta} \quad (4)$$

where, Q_{st} refers to the isosteric heat of adsorption, a differential quantity which is a function of degree of surface coverage or the amount adsorbed, p is the equilibrium pressure of adsorption and T is the temperature and R is the universal gas constant. The isosteric heat is the energy of adsorption obtained from isotherms using Eq. (4). In theory, this is the same as the differential heat but will detect only reversibly adsorbed gas molecules, provided the isosteric heat is constant over a reasonable temperature range [21]. According to Eq. (6), the isosteric heat of adsorption of the pitch-based activated

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