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HYDROGEN ADSORPTION IN CRYOGENIC CONDITIONS: RELATIONSHIP BETWEEN THE POROUS TEXTURE AND THE PARAMETERS OF THE MODIFIED DUBININ-ASTAKHOV EQUATION

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Introduction

Among the wide variety of existing carbons materials, activated carbons (ACs) exhibit, on average, the highest hydrogen adsorption capacities (up to 7 wt. % at 4 MPa and 77 K) [1]. Hydrogen adsorption on ACs is really advantageous at moderate pressures, lower than 40MPa. Thus, the use of ACs can reduce by 23% the volume needed for hydrogen storage when compared to pure compression at 20 MPa and room temperature [2]. Hydrogen adsorption at supercritical conditions on ACs has been adequately fitted with the modified Dubinin-Astakhov (DA) equation. However, the physical meaning of the DA parameters is not completely understood [3] whereas it is of primary importance for designing hydrogen storage systems [4,5].

Materials and Methods

Herein, five commercial activated carbons (CACs) were studied, namely: MSC-30 and MSP20X from MAXSORB®, Kansai Coke and Chemicals TM (Japan); SA1500 and SA20 from Nunchar Ingevity ®; and TH90I from Silcarbon®. Textural characterization of the samples was carried out by N_2 and CO_2 physisorption, at 77 and 273 K, respectively. Prior to sorption isotherms determination, each CAC was degassed under vacuum (< 10^{-1} Pa) at 523 K for more than 24 h. Treatment of the isotherms data was performed to obtain the BET area (A_{BET}). The 2D-NLDFT HS model, applied to both the N_2 and CO_2 adsorption isotherms, was used to determine the NLDFT surface area (S_{NLDFT}), the pore size distributions (PSD)[6] and the volumes of pores with diameter under 0.7 nm ($V_{<0.7,NLDFT}$), between 0.7 and 2 nm ($V_{0.7\text{-}2,NLDFT}$), under 2 nm (V_{micro}) and the total volume of pores, V_T. The volume of mesopores, V_{mes}, was calculated as V_T-V_{micro}. Hydrogen isotherms were obtained at cryogenic temperatures from 77 to 273 K. A precise temperature control (±0.005 K) was carried out through a helium refrigerator with a single-stage closed cycle. Eleven pressures steps for the adsorption branch (0.1, 0.5, 0.8, 1, 2, 3, 5, 7.5, 10, 12.5 and 14 MPa) and five for the desorption branch (11.5, 8, 4.5, 1.5 and 0.5 MPa) were performed. Experimental results were fitted using the modified DA equation with the MATLAB® software.

Results and Discussion

Table 1 shows the textural parameters obtained from the N_2 and CO_2 isotherms data. A_{BET} ranged from ~1200 to ~3310 m^2/g for TH90I and MSC-30, respectively. S_{NLDFT} ranged from ~1260 to ~2220 m^2/g for the same CACs. A high percentage of mesopores was observed for MSC-30, SA1500 and SA20 carbons while the carbons MSP20X and TH90I were essentially microporous. Table 1 also shows the hydrogen capacity of these CACs, expressed as n_{exc} (mol kg^{-1}), which is defined as the difference between hydrogen uptake on the surface of AC at a specific temperature and pressure, and the amount that would be present in the same volume and at the same temperature and pressure in the absence of

the adsorption forces. n_{exc} varied from 2.6 to 5.8 wt. % (at 77K and 4 MPa) and it was directly proportional to S_{NLDFT}.

Table 1. CACs textural properties and hydrogen storage capacities (n_{exc}) at 77K and 4MPa

	A_{BET} m^2/g	S_{NLDFT} m^2/g	V_T cm^3/g	$V_{<0.7,NLDFT}$ cm^3/g	$V_{0.7\text{-}2,NLDFT}$ cm^3/g	V_{micro} cm^3/g	V_{mes} cm^3/g	n_{exc} wt. %
MSC-30	3305	2216	1.60	0.06	0.90	0.96	0.64	5.8
MSP20X	2363	2007	0.93	0.21	0.67	0.88	0.05	4.8
SA1500	2204	1621	1.33	0.05	0.61	0.66	0.67	3.5
SA20	1737	1305	1.20	0.06	0.44	0.50	0.70	3.3
TH90I	1204	1256	0.50	0.22	0.25	0.47	0.03	2.6

The modified DA equation reads as follows:

$$n_{exc} = n_{max} \exp\left(\left(\frac{RT}{\alpha+T\beta}\right)^2 ln^2\left(\frac{P_0}{P}\right)\right) - \rho_g V_a \qquad \text{Equation 1}$$

where n_{max} (mol kg^{-1}) is the amount of adsorbed hydrogen corresponding to the saturation of the entire available porous volume, α (J mol^{-1}) is the "enthalpy" factor, β (mol J^{-1} K^{-1}) is the "entropy" factor [7], P_0 (MPa) is the pseudo-saturation pressure, according to Dubinin definition [8], and V_a (cm^3 g^{-1}) is the volume of the hydrogen adsorbed phase. Table 2 shows these parameters obtained from the fitting of the hydrogen isotherms with the modified DA equation. Figure 1 shows hydrogen isotherms on MSP20X together with the good fitting obtained with the modified DA equation.

Table 2. DA parameters

	n_{max} (mol/kg)	α (J/mol)	β (J/mol K)	P_0 (MPa)	V_a (cm^3/g)
MSC-30	72.5	3300	15.8	1013	1.50
MSP20X	47.4	4094	11.5	632	1.09
SA1500	46.2	3345	13.1	632	0.87
SA20	36.7	3244	13.7	616	0.72
TH90I	26.1	4258	10.7	500	0.56

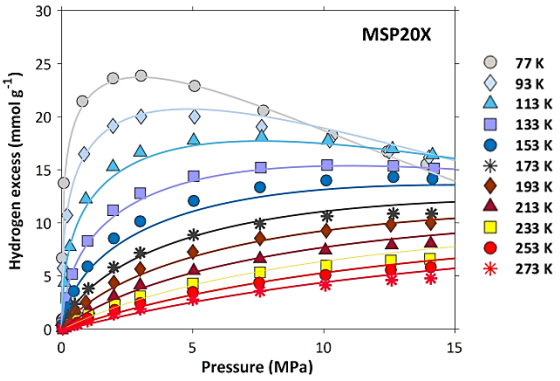

Figure 1. Hydrogen isotherms on MSP20X and their fitting with the modified DA equation.

The parameters α and β are related to the enthalpy, ΔH_a^0, and entropy, ΔS_a , of adsorption, respectively, as follows [7]:

$$\Delta H_a^0 = -\alpha\sqrt{-\ln\left(\frac{n_a}{n_{max}}\right)} \qquad \text{Equation 2}$$

$$\Delta S_a = \frac{-n_{max}\,\beta\sqrt{\pi}}{2}\left[1 - Erf\left(\sqrt{-\ln\left(\frac{n_a}{n_{max}}\right)}\right)\right] + n_a\left[\beta\sqrt{-\ln\left(\frac{n_a}{n_{max}}\right)}\right] + n_a R\, Ln(P^0/P_0) \qquad \text{Equation 3}$$

Figure 2 shows the evolution of V_a and n_{max} with S_{NLDFT}. Both parameters increased with S_{NLDFT}, highlighting the paramount importance of surface area for hydrogen adsorption. Figure 3 shows the β and α parameters as a function of the average micropore size. α, related to the adsorption enthalpy, decreased as the average micropore size increased, due to the stronger interactions between the

hydrogen molecules and the walls within narrow pores. In the case of β, it increased with pore size due to the lower ordering of hydrogen molecules achieved.

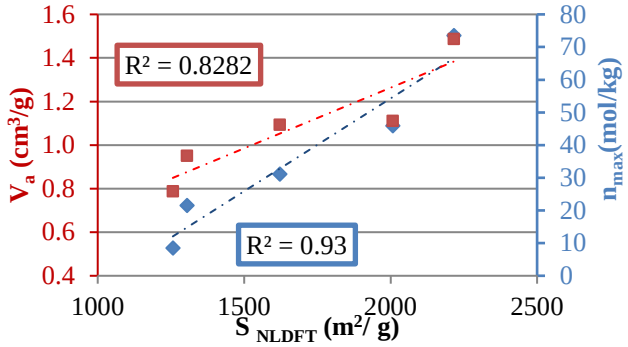

Figure 2. V_a and n_{max} as a function of S_{NDLFT}.

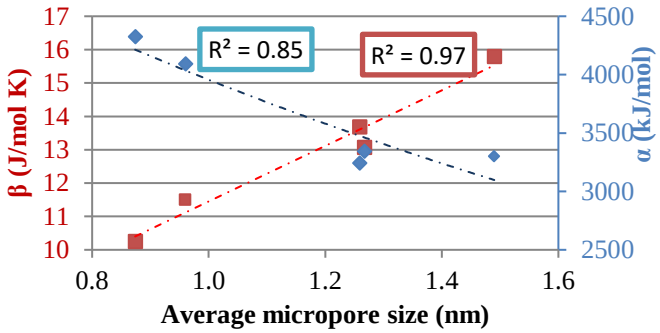

Figure 3. Enthalpy (α) and entropy (β) factors as a function of average micropore size.

Conclusion

The modified Dubinin-Astakhov (DA) equation proved to be a good analytical tool for understanding experimental hydrogen adsorption data over a wide range of pressures and temperatures. The evolution of the DA parameters was correlated to the textural properties of the studied CACs. The entropy factor showed a linear increase with the average micropore size, while the enthalpy factor showed the opposite trend.

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