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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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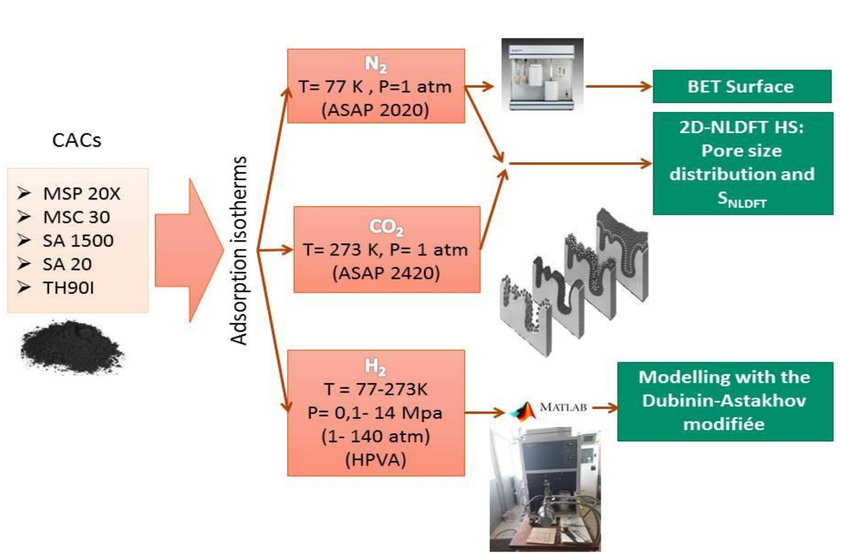
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INTRODUCTION

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) [1,2]. 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 [3]. Hydrogen adsorption at supercritical conditions on ACs has been adequately fitted with the modified Dubinin-Astakhov (MDA) equation. However, the physical meaning of the MDA parameters is not completely understood [4] whereas it is of primary importance for designing hydrogen storage systems [5,6,7].

METHODOLOGY



TEXTURAL PROPERTIES

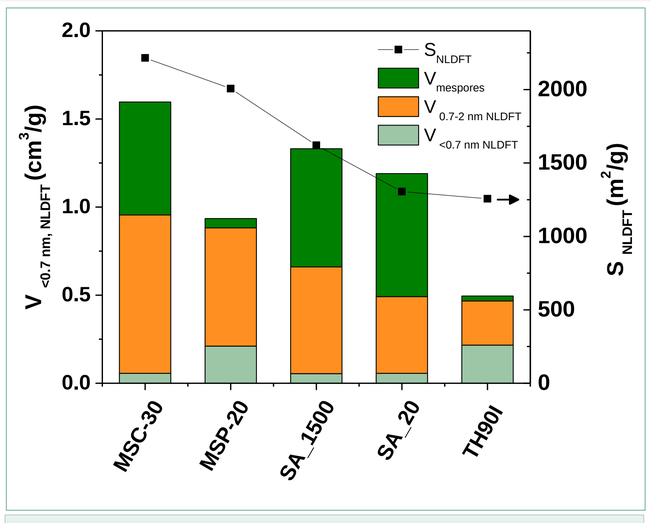


Figure 1. Pore volumes and S_{NLDFT}

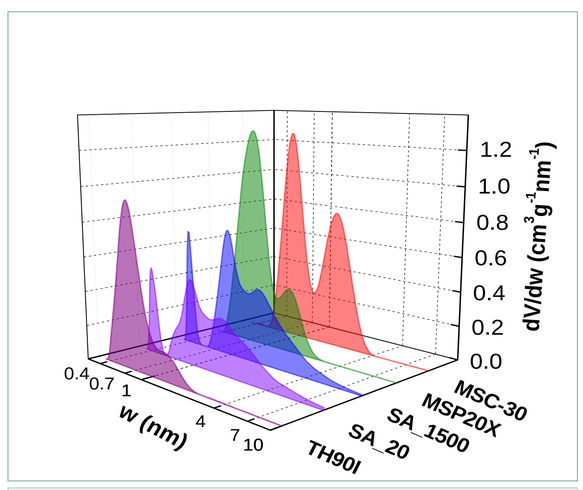


Figure 2. Pore size distributions

A high percentage of mesopores was observed for MSC-30, SA1500 and SA20 carbons while MSP20X and TH90I were essentially microporous.

MODIFIED DUBININ-ASTAKHOV Equation

In order to analyze the relationship between the textural properties and the hydrogen adsorption capacity of these materials, we first fitted the excess hydrogen adsorption with the MDA equation.

DUBININ-ASTAKHOV Model

$$n_{exc} = n_{abs} - \rho_g V_a$$

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

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

$$\Theta = n_{abs}/\, n_{max}$$

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

n_{abs} [mol kg^{-1}]: absolute adsorbed amount of H_2
ρ_g [kg m^{-3}] : adsorbed phase density
V_a [m^3 kg^{-1}] : adsorbed phase volume
n_{max} [mol kg^{-1}]: maximal hydrogen amount
P° [MPa] : saturation pression
α [J mol^{-1}] : enthalpie factor
β [mol J^{-1} K^{-1}] : entropie factor
ΔH_a^0 [kJ mol^{-1}] : adsorption enthalpy
ΔS_a [kJ mol^{-1}] : adsorption entropy
P_0 [MPa] : pseudo saturation pressure
P^0 [MPa] : saturation pressure
R : 8,314 [J mol^{-1} K^{-1}]
Θ : hydrogen fractional filling

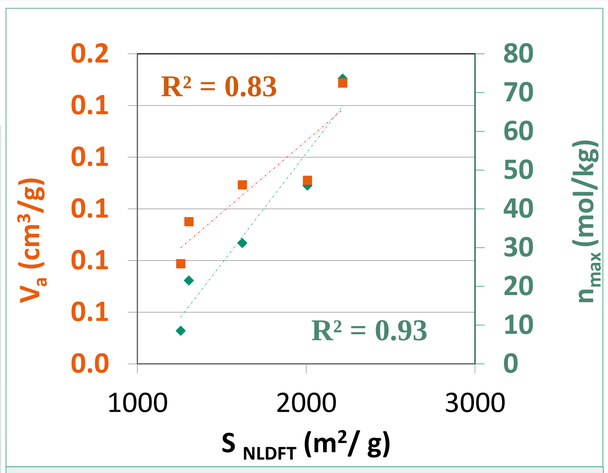


Figure 5. V_a and n_{max} vs S_{NLDFT}

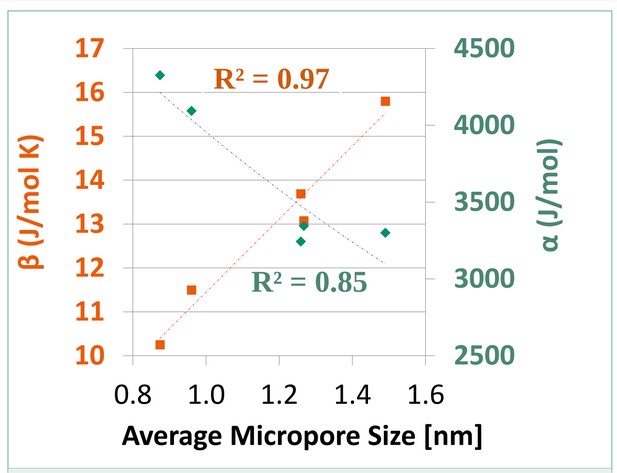


Figure 6. Entropy and enthalpy factors vs average pore size

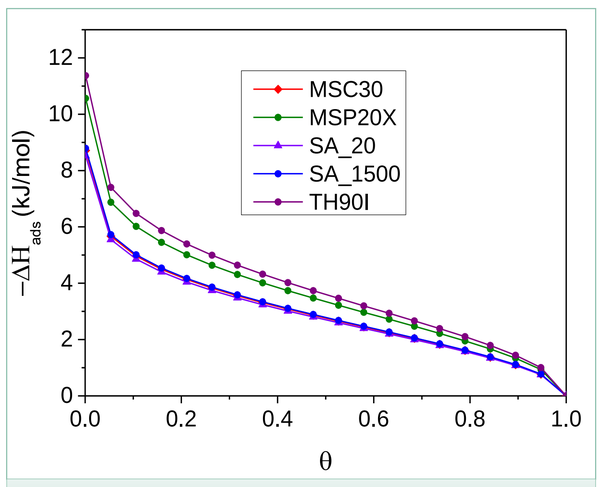


Figure 7. Adsorption enthalpie vs Θ

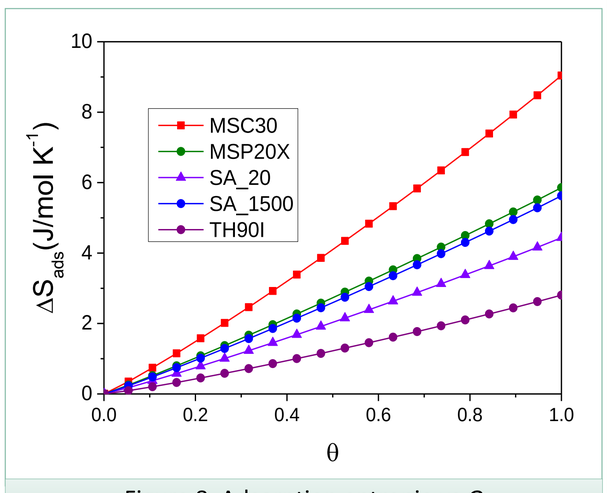


Figure 8. Adsorption entropie vs Θ

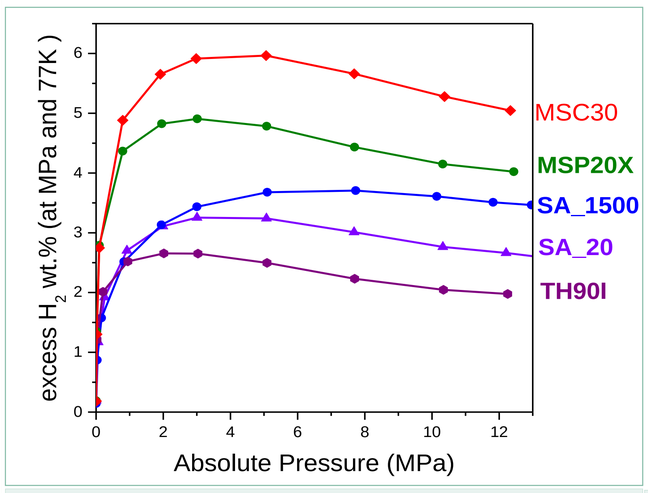


Figure 3. Excess H_2 isotherms at 77 K and 0.1-14 MPa

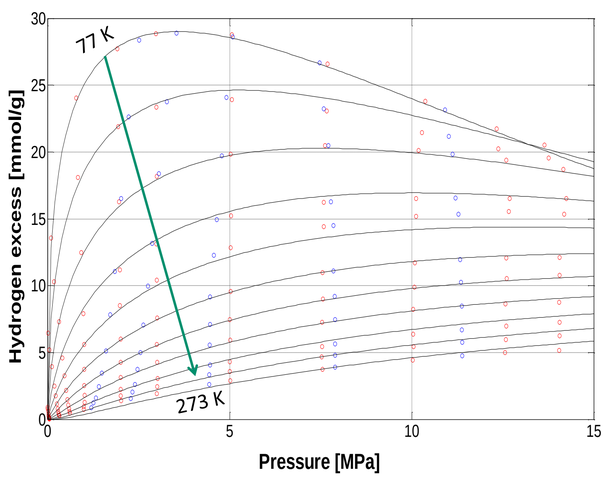


Figure 4. MDA fitting of excess H_2 Isotherms on MSC30

Figure 5 shows that V_a and n_{max} increased with S_{NLDFT}, highlighting the paramount importance of surface area in hydrogen adsorption. Figure 6 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. β increased with pore size due to the lower ordering of hydrogen molecules achieved. Figures 7 and 8 show adsorption enthalpy and entropy as a function of Θ, while the first one decreases the second one increases with fractional filling.

CONCLUSIONS

The modified Dubinin-Astakhov (MDA) 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 MDA 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. Enthalpie and entropie variation with the hydrogen fractional filling were determined for all the CACs.

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