Hydrogen adsorption in cryogenic conditions: relationship between the porous texture and the parameters of the Modified Dubinin-Astakhov equation
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Among the wide variety of existing carbons, 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].

INTRODUCTION

METHODOLOGY

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

\[ n_{\text{exc}} = n_{\text{ads}} - P_h V_a \]

\[ n_{\text{exc}} = n_{\text{max}} \exp \left( \frac{-R T}{\Delta H_f^0} \ln \left( \frac{\rho}{\rho_a} \right) \right) - P_h V_a \]

\[ \Delta H_f^0 = -a - \ln \left( \frac{n_{\text{max}}}{n_{\text{ref}}} \right) \]

\[ \Delta S_a = \frac{n_{\text{max}} \rho^2 R^2}{2} \left( 1 - \ln \left( \frac{n_{\text{max}}}{n_{\text{ref}}} \right) \right) + n_{\text{exc}} \left( \ln \left( \frac{n_{\text{max}}}{n_{\text{ref}}} \right) \right) + n_{\text{exc}} R \ln \left( \frac{P_0}{P_a} \right) \]

Figure 3. Excess H₂ isotherms at 77 K and 0.1-1.4 MPa

Figure 4. MDA fitting of excess H₂ isotherms on MSC30

Figure 5 shows that \( V_a \) and \( n_{\text{exc}} \) increased with \( S_{\text{SBET}} \) highlighting the paramount importance of surface area in hydrogen adsorption. Figure 6 shows the \( \beta \) and \( \alpha \) parameters as a function of the average micropore size. \( \alpha \), 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. \( \beta \) 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 \( \Theta \), 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. Enthalpy and entropie variation with the hydrogen fractional filling were determined for all the CACs.

REFERENCES


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