SUPPORTING INFORMATION

Micropore Filling and Multilayer Formation in Stöber Spheres Upon Water Adsorption

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Ideal micropore filling: adsorption isotherms and Dubinin-Radushkevich representation Ideally, the filling of microporosity only depends on the isosteric heat associated to the interaction micropore-adsorbate (E_{ads}), as the decisive system parameter, and the ambient temperature (T). The corresponding adsorption isotherm proceeds until the accessible (able to be filled) micropore volume (V_{micro}) is completed. The DR equation provides a useful representation, in which the adsorbed volume V and the relative pressure V - p/p_0 are correlated according to a linear relationship (Eq. (1) in main text). The DR equation contains the parameters that, in the ideal case, fully determine the microporosity filling. In most experiments, the adsorption temperature is constant or varies in a narrow range, so it can be assumed that the system parameters (E_{ads} and V_{micro}) remain unchanged. In this case, the micropore filling is expected to follow the thermodynamic criterion: adsorption, or pore filling, is facilitated at low T, as vapor molecules with low kinetic energy become more easily bonded or condensed, while it is increasingly hindered at higher T. This thermodynamic trend is expressed in the slope of the linear DR data, which increases proportionally to T^2 (Eq. (2) in main text). Since an ideal, non-restricted micropore filling is perfectly reversible, the emptying of the microporosity will follow the same thermodynamic tendency.

It is illustrative to consider the expected temperature-dependence of the adsorption isotherm and the associated DR plot (Figure S1). Therefore, we have simulated the adsorption data according to Eq. (1), setting E_{ads} = 6 kJ/mol and V_{micro} = 0.050 cm^3/g as constants. The adsorption isotherms (Figure S1a) were generated by rearranging Eq. (1) into:

$$V = V_{micro} exp\left(-0.435\, A \ln^2\left(\frac{p}{p_0}\right)\right). \qquad \text{(S1)}$$

Figure S1a shows the simulated isotherms for the same temperature range used in this work (T = 10 – 60 ºC). According to the expected trend, the progressive difficulty for adsorption by increasing T is manifested by a decreasing adsorbed amount V at any given relative pressure, so that the isotherm growth becomes flatter. Correspondingly, the slope in the DR plot is gradually steeper (Figure S1b). Nevertheless, in the assumed case of ideal micropore filling, the same volume V_{micro} is eventually filled, regardless of the temperature (asymptotic value in Figure S1a and y-intercept in Figure S1b). Any experimental deviation from this behavior would indicate that the tested system departs from the assumed conditions of unrestricted micropore filling, as discussed in Section 3.2.

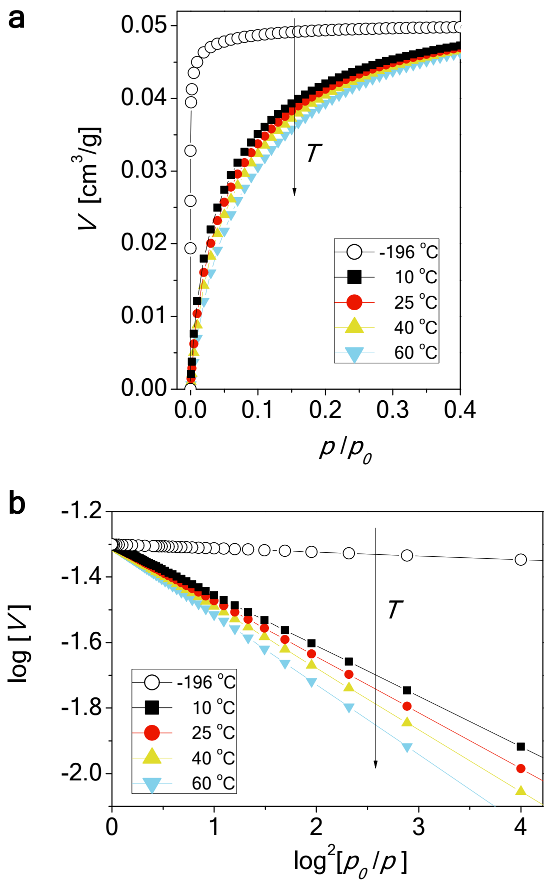

Figure S1. Simulated adsorption isotherms (a) and associated DR plot (b) for simple micropore filling at different temperatures T. Data were generated using Eq. (S1) with constant E_{ads} = 6 kJ/mol and V_{micro} = 0.050 cm^3/g.

For sake of comparison, we also simulate the adsorption data for T = –196 ºC (open symbols in Figure S1), which is the standard operational temperature of N_2 adsorption experiments. At this cryogenic temperature, the adsorbing molecules possess a very low kinetic energy, which greatly facilitates the filling of the microporosity. This fact leads to an abrupt increase in the adsorbed volume at very low pressures (Figure S1a), which is a typical signature of the presence of microporosity in N_2 adsorption measurements (if no kinetic restrictions are present, as in the case of Stöber spheres**Error! Bookmark not defined.**). The corresponding DR plot would exhibit a very flat straight line (Figure S1b).

Adsorption beyond micropore filling: Dubinin-Radushkevich representation A most useful aspect of the DR data representation is that any adsorption contribution additional to the micropore filling is reflected as a superlinear behavior of the adsorption data. In Figure S2a we consider an adsorption isotherm, which results from pure micropore filling (with same parameters taken above, and T = 25º) and a further contribution due to e.g. multilayer adsorption on external surfaces –the latter is assumed to occur only above p/p_0 = 0.7 (inset in Figure S2a). The total isotherm, when compared to that corresponding solely to micropore filling, exhibits a continuous deviation above p/p_0 = 0.7 (Figure S2a). The associated DR plot shows how the adsorption data behave linearly until p/p_0 = 0.7 and superlinearly at higher pressures (Figure S2b). Note that the adsorbed volume V at which the superlinearity begins is inferior to V_{micro} (linear extrapolation in Figure S2b). This fact is implicitly produced by the DR theory, which assumes that the micropore volume is only completed at the saturation gas pressure (p/p_0 = 1) –see Eq. (1) in main text. (For cryogenic temperatures, or very high E_{ads}, the DR slope is very small, and any additional adsorption process would induce superlinearity at a volume V very close to V_{micro}, being difficult to distinguish.

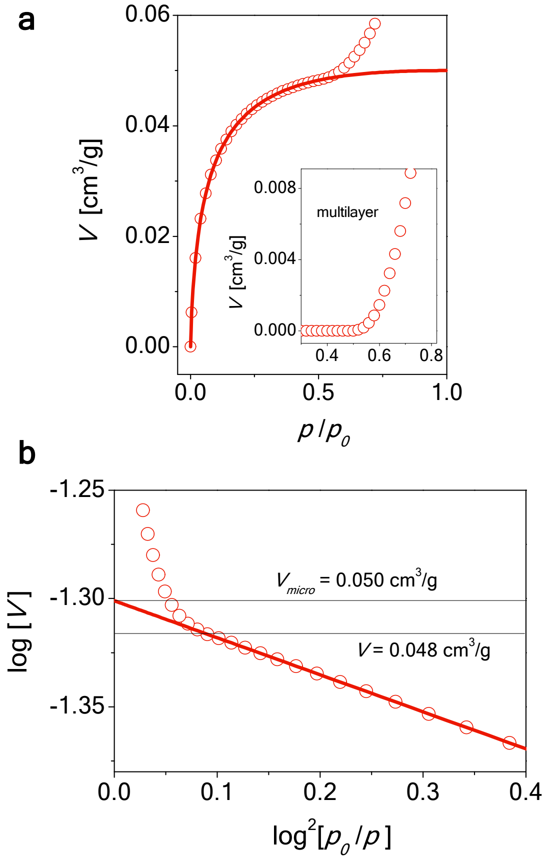

Figure S2. Simulated adsorption isotherms (a) and associated DR plot (b) resulting from the sum (empty circles) of two contributions: micropore filling and an additional contribution, such as multilayer formation. Micropore filling data (red lines) are the same as in Figure S1 for T = 25 ºC. The multilayer formation is assumed to begin at $p/p_0 = 0.5$ (solid circles, inset in (a)).