**Electronic Supplementary Information (ESI)** 

## High performance microspherical activated carbons for methane storage and landfill gas or biogas upgrade

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## Analysis of $\alpha_s$ plots

The  $\alpha_s$  plots present the characteristic features of the presence of different types of micropores: two well-defined linear regions, both with positive interception and a breakdown point at  $\alpha_s \approx 1.^1$ As described in Figure S1, the total micropore volume ( $V_{\alpha \text{ total}}$ ), was obtained, as usually, by back extrapolation of the high relative pressure region ( $\alpha_s > 1$ ). The ultramicropores (width<0.7 nm) volume,  $V_{\alpha \text{ ultra}}$ , was evaluated by the intercept of the linear range defined by the experimental points determined at  $p/p^0$  between 0.02 and, about, 0.4. The volume of the larger micropores, supermicropores (width>0.7 nm),  $V_{\alpha \text{ super}}$ , is the difference  $V_{\alpha \text{ total}} - V_{\alpha \text{ ultra}}$ .



Figure S1. Hypothetical  $\alpha_s$  plots for microporous adsorbents.

## Adsorption modeling

An established methodology has been used for the calculation of the adsorption of binary mixtures of gases.<sup>2</sup> Briefly, it involves determination of an equation of state for the Gibbs free energy of desorption which was calculated from the pure gas adsorption isotherms. For these calculations it is useful to have the experimental data described by an analytical expression, for example in this work a Virial equation has been used:

$$p = \frac{n^{ads}}{K} \exp\left(C_1 n^{ads} + C_2 n^{ads^2} + C_3 n^{ads^3}\right)$$
(1)

Where, *K* is the Henry constant and  $C_1$ ,  $C_2$  and  $C_3$  are the respective Virial coefficients. The integration of equation 1 will give the free Gibbs energy of desorption, as follows:

$$G = RT \int_{0}^{p} \frac{n^{ads}}{p} dp = RT \left( n^{ads} + \frac{1}{2}C_{1}n^{ads^{2}} + \frac{2}{3}C_{2}n^{ads^{3}} + \frac{3}{4}C_{3}n^{ads^{4}} \right)$$
(2)

In this equation the adsorbed amount  $n^{ads}$  and the Gibbs free energy *G* are functions of temperature and pressure, i.e., n(T, p) and G(T, p). The composition of the adsorbed and gas phases of mixtures may be estimated using the ideal adsorbed solution theory (IAST) and the Gibbs free energy for the pure components (Equation 2). This theory assumes that the mixing of the adsorbed phases of the two components is ideal, although activity coefficients may also be estimated from adsorption isotherms of mixtures to account for non-ideal behavior. These non-idealities arise mainly due to adsorbate-adsorbate interactions and are often less dominant than adsorbate-adsorbent interactions already accounted by IAST. If different equations were used to describe the adsorption data (Langmuir or Langmuir–Virial for example) equations 1 and 2 would be different, but the methodology would be the same and the equations from this point onwards remain unchanged.

The standard state for forming adsorbed solutions from the pure components is the free Gibbs energy of the pure components. According to IAST, the equilibrium condition is described by the three simultaneous equation set:

$$G_{1}(n_{1}^{0}) = G_{2}(n_{2}^{0})$$

$$py_{1} = p_{1}(n_{1}^{0})k_{1}$$

$$py_{2} = p_{2}(n_{2}^{0})k_{2}$$
(3)

were  $y_i$  and  $x_i$  are the gas and adsorbed molar factions of component *i*. The calculations were made by numerically solving the equation system 3. For this, equation 2 had also to be numerically solved to determine the standard-state loadings  $(n_i^0)$  for each one of the two pure gases (1 and 2) at a given value of *G* (in this case  $G_1=G_2$ ). The components molar fraction in the gas  $(y_i)$  and adsorbed phases  $(x_i)$  is calculated, for plotting the phase equilibrium diagrams. With this method various phase diagrams can be calculated.

The total adsorbed amount n in a material, at a given temperature and pressure, is calculated by the equation:

$$\frac{1}{n} = \frac{x_1}{n_1^0} + \frac{x_2}{n_2^0} \tag{4}$$

were the  $x_i$  and  $n_i^0$  are determined by solving equation 3.

The individual loadings  $(n_i)$  of each component is then calculated by:

$$n_i = nx_i \tag{5}$$

The selectivity values (separation factor), for a given binary gas phase composition and pressure, can be calculated, at constant pressure and temperature, and assuming the ideal behavior, by the difference in pure-component Gibbs free energy:<sup>3</sup>

$$G_{2} - G_{1} = RT \int_{0}^{1} \left[ \frac{n_{1}^{ads}}{y_{1}} - \frac{n_{2}^{ads}}{y_{2}} \right] dy_{1} \approx \overline{n}^{ads} RT \ln(S_{1,2})$$
(4)

Equation 4 may be used, at high pressures, to estimate the mean selectivity (S) at constant pressure and temperature, by  $\ln(S_{1,2}) = G_2 - G_1/\overline{n}^{ads}RT$ , were  $G_1$  and  $G_2$  are the Gibbs free energy of component 1 and 2, in the same solid adsorbent,  $\overline{n}^{ads}$  is the mean adsorbed amount, and  $y_1$ ,  $y_2$  are the molar fractions of component 1 and 2 in the gas phase. The detailed procedure for calculating  $G_1$  and  $G_2$  is described elsewhere.<sup>4</sup> During calculations of selectivity, the preferentially adsorbed component is always considered as component '1' and written first while referring to binary mixture *e.g.*  $CO_2/CH_4$  binary mixture as,  $CO_2$  get adsorbed more selectively then  $CH_4$ .



Figure S2 - Methane and carbon dioxide adsorption isotherms in the low pressure region at 25 °C on the three activated carbon samples.

## References

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