

Supplementary Information

Influence of Sample Preparation on IGC measurements: The Cases of Silanised Glass Wool and Packing Structure

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Deconvolution of the Surface Energy Distributions

The computational method for the deconvolution of surface energy distributions used in this paper is based on the work by Smith et al. on the prediction of surface energy distribution of crystalline materials based on the FD-IGC data.^{1,2} It is an iterative optimisation algorithm reproducing, *in silico*, the adsorption experiment, again and again, until it finds a surface energy distribution fitting the experimental data well. This method has been described by Smith et al., but in this work an improved version of it is employed.

In this study, it was assumed that the surface energy distribution (χ) is constructed from the sum of four Gaussian distributions, each one corresponding to an adsorption site of particular surface energy (μ). This assumption is formulated mathematically by the following equation:

$$\chi = \sum_{i=A}^4 \frac{w_i}{\sigma_i \sqrt{2\pi}} e^{-\frac{1}{2} \left(\frac{\gamma_i^d - \mu_i}{\sigma_i} \right)^2} \quad (Eq. S1)$$

In equation S1, i is the particular adsorption site, w is the relative contribution of the particular adsorption site and σ is the variance of the surface energy of the adsorption site (in this study a fixed value of 1 mJ/m² was assigned to it for all the adsorption sites). At the beginning of the computational algorithm initial guesses for every value of w_i and μ_i are assigned by the operator. It is important to note that the sum of the values of w_i 's should be equal to unity.

This study, goes a step beyond previous work^{1,2} introducing a BET equation to describe the adsorption process. This type of isotherm accounts for multilayer adsorption and it collapses to ????. However, other isotherms can be employed. The general form of this isotherm is given by the simple linear relation:

$$\theta = \frac{C \left(\frac{P}{P_0} \right)}{\left(1 - \left(\frac{P}{P_0} \right) \right) * \left(1 + C \left(\frac{P}{P_0} \right) - \left(\frac{P}{P_0} \right) \right)} \quad (Eq. S2)$$

In equation S2, θ is the fractional coverage, C is an adsorption exponential constant, P_0 is the saturation pressure and P is the pressure. The constant value is given by:

$$C = \frac{v_0}{n_0 \sqrt{2\pi m k T}} \exp \left(\frac{-\Delta G_{ads}}{k T} \right) \quad (Eq. S3)$$

In equation S3, v_0 corresponds to the Mean Stay Time of an adsorbed molecule on the surface i.e. it measures the tendency of the molecules to desorb, n_0 stands for the concentration of surface sites, m is the mass of an adsorbed molecule, ΔG_{ads} is the adsorption surface energy, k is the Boltzmann constant and T the temperature. Since the adsorbent molecule is a van der Waals fluid with negligibly small polar component, then the energy of adsorption is given by equation S4:

$$\Delta G_{ads} = -2a_m \sqrt{\gamma_{surface}^{LW} \gamma_{adsorbate}^{LW}} \quad (Eq. S4)$$

The term a_m is the molecular cross sectional area of the alkane and the $\gamma_{adsorbate}^{LW}$ term is its surface energy. Table S1 summarizes their values, as they were used in this work, for octane, nonane and decane.

Table S1 The values of molecular cross sectional area and surface energy used in the model for the three alkanes.

Alkane	Cross sectional area (\AA^2)	$\gamma_{adsorbate}^{LW}$ (mJ/m ²)
Octane	58.1	20.67
Nonane	64.4	21.79
Decane	70.7	22.91

Using equations (S1-S4) and data in Table S1, it is easy to calculate the corresponding experienced energy E for every alkane at each value of surface coverage, by simply solving the following integrals in a range of surface energies (ε):

$$E = \int_0^{\infty} \theta * \chi * \varepsilon * d\varepsilon \quad (Eq. S5)$$

The experienced energy calculated, for each alkane at each value of surface coverage, is then implemented on a Schultz plot in order to calculate the actual surface energy measured at every value of surface coverage.³ This process is repeated in every value of surface coverage. This allows the reconstruction of a surface energy map, the same as those obtained from IGC measurements. The calculated surface energy map is compared with the experimental one. If they do not agree, the input values for w_i and μ_i are adjusted until the experimental and the computational values converge. In a Matlab environment, the fsolve command provides a sufficient optimisation algorithm for this, but can only be done manually. In any case, the operator should always be aware to check how realistic are the results produced from the model.

References:

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