Determining the surface area of solids using the BET equation

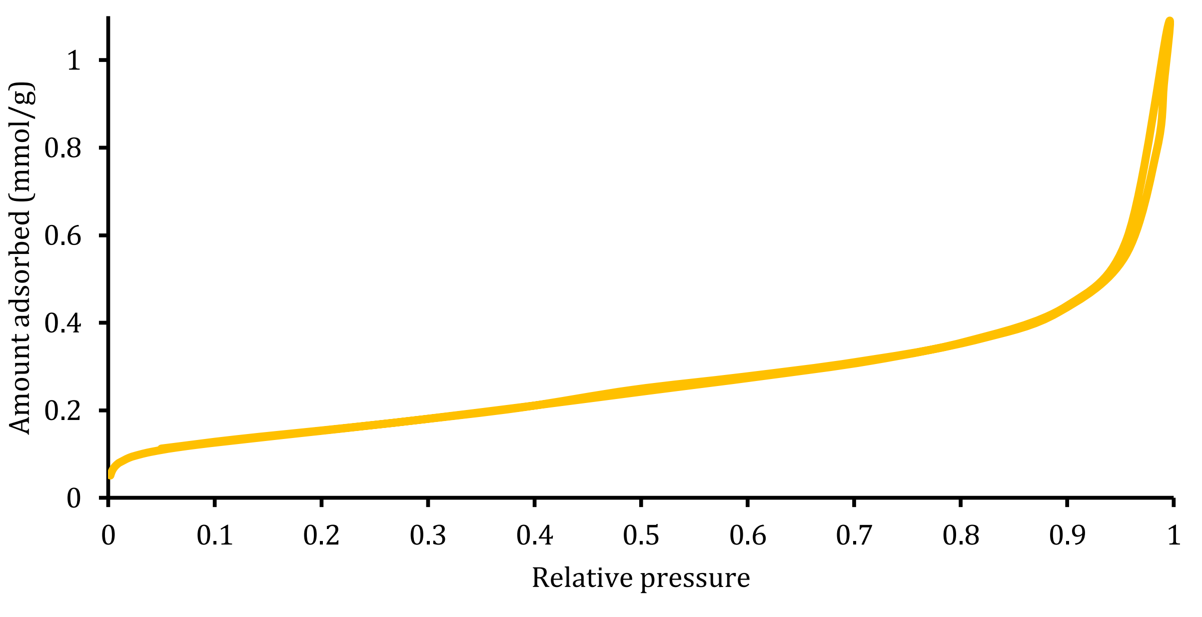
Introduction

The surface area of a solid is defined as the external and the accessible internal pore surfaces. **It is widely used to characterise materials for adsorption, catalysis and reactions on surfaces, as its value represents the number of potential active sites.** The surface area is estimated using the Brunauer, Emmett & Teller (BET) equation, from a specific region of a gas adsorption isotherm where monolayers of adsorbate are considered to take place.

The gas adsorption isotherm is experimentally obtained as follows. Successive doses of an adsorptive gas probe, typically N_2 at 77 K, are sent to the solid material, preliminarily dried and evacuated. The amount of gas molecules that can adsorb onto the surface of the solid is derived from the evolution of the pressure in the system. The cumulative amount of adsorbate plotted with respect to the pressure is the adsorption isotherm.

Experimental details

- Method: determination of the BET specific surface area of solids by gas adsorption, ISO 9277:2010(E) [1]
- Instrument: *Micromeritics* 3Flex
- Adsorptive gas: N_2 at 77 K
- Sample: TiO_2, dried for 3 h at 150 °C under vacuum (unrestricted from $1.33 \cdot 10^{-2}$ mbar)
- Amount of sample: 620 mg
- Sample holder: glass tube of 12 mm outer diameter with a seal frit



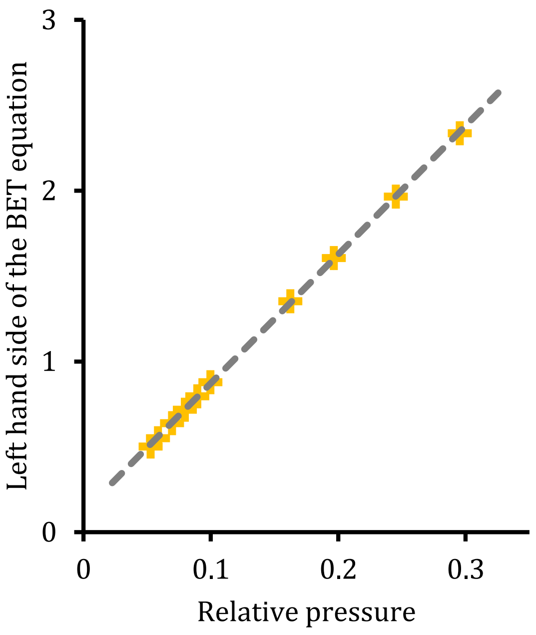
Adsorption isotherm of a titanium dioxide powder. According to the classification of standard physisorption isotherms by the IUPAC [2] this is a type II isotherm: it is characterised by a regular increase of the amount adsorbed over the whole pressure range, with a bend at low pressures. The BET equation is only valid on this type of isotherms and on type IV, associated with mesoporous adsorbents, so long as the hysteresis appears at a relative pressure higher than 0.3.

Results

Brunauer, Emmett & Teller developed a model for type II isotherms, which considers that gas molecules are adsorbed in monolayers, i.e. monomolecular layers. In the specific relative pressure range from 0.05 to 0.30 each monolayer evenly covers the previous one. By applying Langmuir theory to those monolayers they obtained the following BET equation [3]:

$$\frac{P}{n_a(1-P)} = \frac{1}{n_m C} + \frac{C-1}{n_m C} P$$

With n_a the amount of gas adsorbed and P the relative pressure, i.e. respectively the ordinate and abscissa of the adsorption isotherm; n_m is the monolayer amount and C the so-called BET parameter. If the left hand side of the BET equation is plotted with respect to the relative pressure, a linear trend is obtained in the pressure range mentioned above, as shown on the right. According to the equation, the parameters n_m and C are derived from the slope and intercept by linear regression.



The surface area is then estimated from the monolayer amount n_m and the cross-sectional area of a molecule of adsorbate [1]. The BET surface area is finally 12.73 ± 0.06 m^2/g, typical of TiO_2 powder [1].

Conclusion

- The surface area of a solid can be estimated using the BET equation derived from a gas adsorption isotherm, by considering the formation of monolayers of adsorbate.
- The BET model is only valid if the adsorbent is non-porous, macroporous, or mesoporous with wide pore diameter.
- A large quantity of solid is needed: at least several hundreds of mg and it needs to be known within 2 % error, as the results are always presented in specific units.
- The adsorbent must have been dried beforehand (by heating under vacuum or dry gas sweeping) in order to remove from the surface any adsorbed molecule.

[1] Determination of the specific surface area of solids by gas adsorption — BET method, ISO 9277:2010(E)

[2] Sing K.S.W., Everett D.H., Haul R.A.W., Moscou L., Pierotti R.A., Rouquérol J. and Siemieniewska T., IUPAC Recommendations 1984: Reporting Physisorption Data for Gas Solid Systems with Special Reference to the Determination of Surface Area and Porosity, *Pure & Applied Chemistry* 57, 1985, pp. 603-319

[3] Rouquérol F., Luciani L., Llewellyn P., Denoyel R., and Rouquérol J., *Texture des matériaux pulvérulents ou poreux*, Techniques de l'ingénieur P1050