



MEASURING SURFACE AREAS IN CATALYSTS

This Altamira Note gives a basic background on the measurement of BET surface area as applied to catalysts and catalytic supports as well as discusses the flow techniques for measurement of surface area.

Surface Area

The total surface area of a catalyst is perhaps one of the most basic properties of catalysts. Although several methods exist for measuring the surface area, the so-called BET method is almost universally used with common catalytic materials. The technique is named after the authors of the paper describing the equation (Brunauer, Emmett, and Teller, J. Am. Chem. Soc., 60, 30 (1938)) and is based on the physical adsorption of a non-selective gas at low enough temperature to cause the condensation of the adsorbate on the surface. The trick to determining the surface area is to measure when exactly one monolayer of the gas has been adsorbed on the surface. At monolayer coverage the surface area of the solid is given by Equation 1:

$$\text{Surface Area} = a \cdot (V_m/V_M) \cdot N_{Av0}$$

where: V_m is the volume of the adsorbed monolayer;
 V_M is the molar volume of the adsorbate;
 N_{Av0} is Avogadro's number; and a is the cross sectional area of a single molecule of the adsorbate

Nitrogen gas, with a cross sectional area of 16.2 Å, is typically used in BET measurements.

The experimental procedure involves measuring the uptake of adsorbate as a function of partial pressure and plotting the resulting data in the form of the BET equation, viz.:

$$\frac{P_A}{V_T (P_{A(V.P.)} - P_A)} = \frac{1}{V_m C} + \frac{(C-1)}{V_m C} \times \frac{P_A}{P_{A(V.P.)}}$$

Where: P_A is the pressure at which the measurement was taken;
 $P_{A(V.P.)}$ is the vapor pressure of the adsorbate at the temperature of the measurement;
 V_T is the total volume adsorbed; and C is a constant.

The BET equation is of the form of a straight line so that a plot of:

$$\frac{P_A}{V_T(P_{A(V.P.)} - P_A)} \quad \text{versus} \quad \frac{P_A}{P_{A(V.P.)}}$$

results in a straight line with a slope equal to $(C-1)/V_m C$ and an intercept equal to $1/V_m C$. The monolayer volume is thus $V_m = 1/(\text{slope} + \text{intercept})$, and the surface area can be directly calculated from Eq. 1.

How Applicable is the BET Equation?

In 1940 Brunauer published his now famous classification of adsorption isotherms (Brunauer, Deming, Doming, and Teller, J. Am. Chem. Soc., 62, 1723 (1940)). He divided all isotherms into five classes, depicted in Figure 1, according to their general shape.

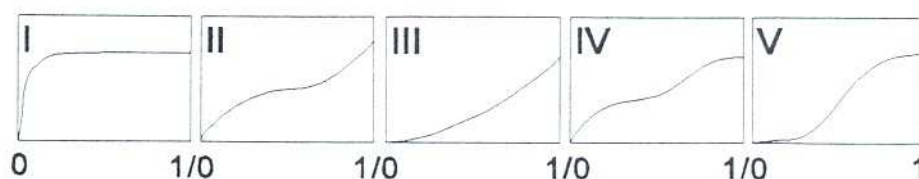


Figure 1. Brunauer's classification of isotherms

Type 1, is typically exhibited by microporous adsorbents in which the average pore size is not much larger than the molecular diameter of the adsorbate; this type is commonly observed with zeolites. Types II and III are seen with adsorbents having a wide range of pore sizes, ranging from micropores to macropores where sorption proceeds from monolayer adsorption, to multilayer, and finally to condensation. The Type II isotherm is the one that is most often observed in supported catalysts. Types IV and V are less common. A Type IV isotherm suggests a bimodal pore network where two surface layers may be formed. Type V is encountered when the adsorbate exhibits large intermolecular effects.

The BET equation works well for Type II and Type IV isotherms within a small range of partial pressures, typically $P_A/P_{A(V.P.)} \leq 0.3$. The equation does not work well for Type III or Type V isotherms. For Type I isotherms, an apparently accurate value of surface area can be obtained from the BET equation, but its physical meaning is questionable since no multilayer adsorption can occur. Indeed, for microporous materials other equations, such as the Dubinin-Radushkevich equation, better describe the adsorption process. We discussed the characterization of microporous materials in the Altamira Note of September, 1991.

Flow Technique for Measuring the BET Surface Area

Altamira's characterization units allow for the dynamic measurement of surface area. Using this technique, single or multi-point determinations of the surface area of catalysts or catalysts supports can be rapidly made. The Altamira flow technique is an extension of the standard ASTM single-point method D-4567 and contains aspects of the ASTM multipoint method D-3663. A representation of the experiment is shown in Figure 2. Nitrogen and helium are blended using precise flow regulators to different partial pressures and passed, at constant flow, over the solid of interest. A thermal conductivity detector (TCD) constantly monitors the signal. After a steady signal is reached, the sample is rapidly immersed in liquid nitrogen. This results in the adsorption of nitrogen from the gas stream and a change in the signal corresponding to the loss of nitrogen being adsorbed. The signal will again stabilize as the surface and the gas phase reach equilibrium. At this point the liquid nitrogen is removed and the sample plunged into a water bath in order to desorb the adsorbed nitrogen. The gas stream now becomes rich in nitrogen and this is reflected in the TCD signal. This procedure can be repeated for various N_2 partial pressures.

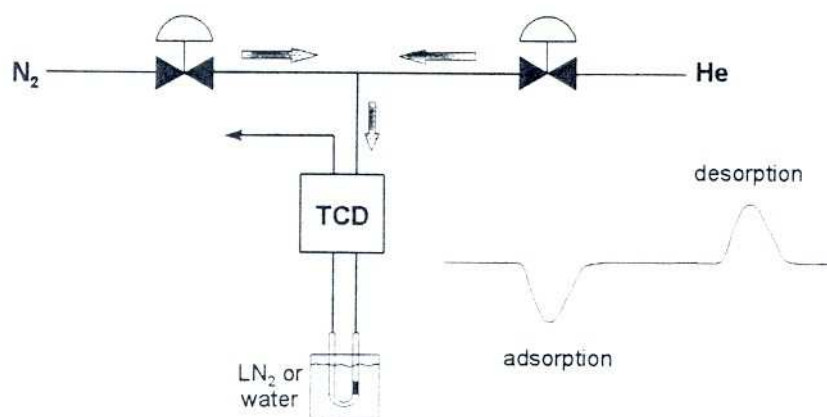


Figure 2. Flow experiment for measuring surface area

The flow technique is a fast, easy, and direct method for determining surface areas. The ratio of N_2 to He in the gas blend corresponds to the partial pressure of nitrogen and this can be readily changed to obtain different points in the isotherm. The area under the adsorption or desorption signal represents the amount of nitrogen that was adsorbed at that particular partial pressure. From a series of such measurements, the BET equation can be fitted and a value of surface area readily obtained.

As with all techniques there are limitations. Isotherm shape and microporosity are two that we have already mentioned. Although in theory, the signal areas corresponding to the adsorption and desorption of the nitrogen are supposed to be identical, we find that for materials containing a significant numbers of micropores (i.e., smaller than 20 Å) the adsorption can be slow and difficult to be accurately measured. For this reason, the desorption areas are preferred for fitting the BET equation. Finally, the technique works best for a range of surface areas. Nitrogen as an adsorbate works best for surface areas in the range of 10 - 400 m^2/g . Surface areas much larger than 400 m^2/g tend to include a large fraction of micropores with its resulting measurement problems; while surface areas less than 10 m^2/g are approaching the limit of

detection for nitrogen. For the latter, krypton can be used as an adsorbate. Its lower vapor pressure at liquid nitrogen temperature and its larger atomic size increase the range of the technique.