APPNOTE 3-01

Measuring surface areas in catalysts

3P INSTRUMENTS
Characterization of
particles · powders · pores

Introduction

This article will give basic background information about the techniques used in determining BET surface area and the use of this data for evaluating catalysts and catalytic supports and substrates. As the determination of BET surface area as well as material characterization by means of physisorption has been covered in a variety of other application notes and publications, this article will instead focus on the dynamic flow method for surface area determination.

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 [1] and is based on the physical adsorption of a non-selective gas at a temperature that is low enough to cause the condensation of the adsorbate on the surface. The trick to determine the surface area is to measure when exactly one monolayer of the gas has been adsorbed on the surface. When a monolayer coverage is obtained, the surface area of the solid is given by this Eq. 1:

$$Surface\ area = a \times \frac{V_m}{V_M} \times N_{avo} \qquad \text{(Eq. 1)}$$

with

V_m...volume of gas in the adsorbed monolayer
V_M...molar volume of the adsorbate
N_{avo}...Avogadro's number
a...cross sectional area of a single molecule of the adsorbate

The most common used gas for BET-analysis is nitrogen gas cooled down to 77.4 K by liquid nitrogen which has a cross sectional area of 16.2 $Å^2$. It stands to note, that since its inception, the reliance of this method on nitrogen at 77 K has been challenged for various reasons. Mainly, the suitability of the two-atomic gas nitrogen with good polarizability and high quadrupole moment has been questioned and guidelines have been established for using different gases such as argon at 87 K and analytical instrumentation has since been developed to accommodate the need for variable temperature ranges in analysis conditions [2,3]. However, though these issues need to be kept in mind, they are not the focus of this article.

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.:

$$\frac{p}{V_T \times (p_0 - p)} = \frac{1}{V_m \times C} + \frac{(C-1)}{V_m \times C} \times \frac{p}{p_0} \qquad \text{(Eq. 2)}$$

with

p...pressure at which the measurement was taken
p_0...vapor pressure of the adsorbate at the temperature of the measurement
V_T...total volume adsorbed
C...constant

The BET equation is written in a linear form so it can be plotted:

$$\frac{p}{V_T \times (p_0 - p)} \; vs. \frac{p}{p_0} \qquad \text{(Eq. 3)}$$

This results in a straight line with a slope equal to (C-1)/V_mC and an intercept equal to 1/V_mC. The monolayer volume is thus V_m = 1/(slope + 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 [4]. He divided all isotherms into five classes according to their general shape (depicted in Fig. 1).

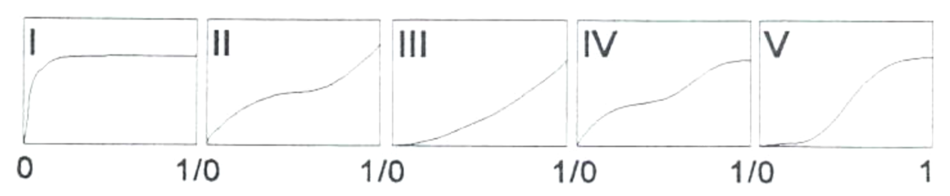

Figure 1 *Brunauer's classification of isotherms [4]*

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/p_0 around 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 models, such as the Dubinin-Radushkevich equation [5], are able to describe the adsorption process better.

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 flow technique used for chemisorption and applied on physisorption 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 Fig. 2. Nitrogen and helium are blended using precise flow regulators to different partial pressures and passed, at constant flow, over the sample. 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.

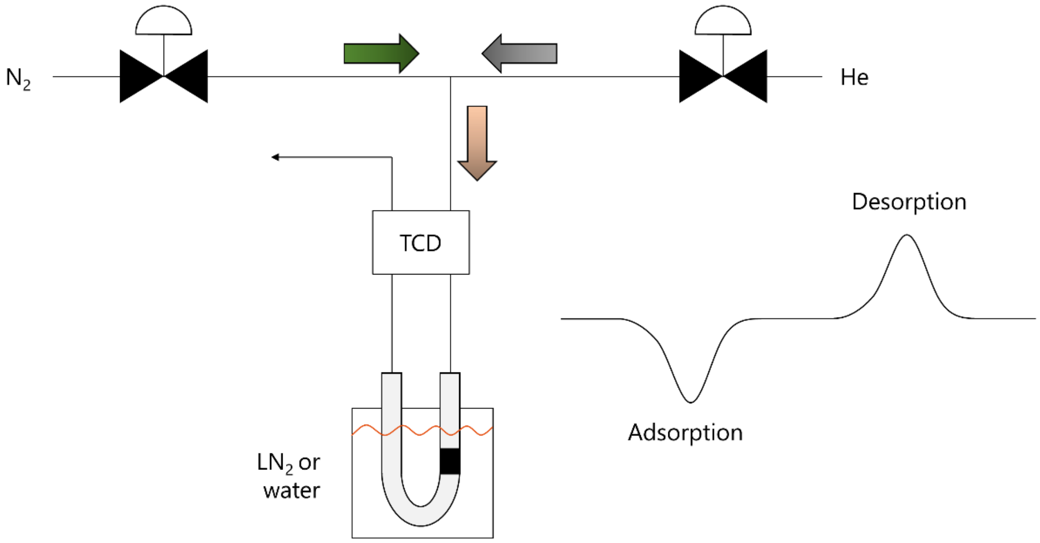

Figure 2 *Flow experiment for measuring surface area*

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 number 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. It has to be noted, that surface areas much larger than 400 m^2/g tend to include a large fraction of micropores with its resulting measurement problems.

Conclusion

Chemisorption analysis stations, which operate with dynamic flow methods and TCD sensors are capable of performing BET surface analysis. The increase speed of the analysis by means of dynamic flow approaches has also led to the development of dedicated surface analyzers for performing rapid single- and multi-point measurements. However, due to the limitations of the dynamic flow method with regards to very small surface areas or very high surface areas in microporosity, these instruments cannot fully be replaced by the static volumetric analyzers with turbomolecular vacuum systems and pure gas adsorption of different adsorbates for special or targeted applications such as Krypton analysis or micropore pore size distributions with Argon.

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References

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