Surface Parameters of Stannic Oxide in Powder, Ceramic and Gel Forms by Nitrogen Adsorption Techniques[1]

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It is now commonly accepted that certain electrical properties of materials may depend upon their surfaces (Mark, 1964; Glemza, 1965). This is especially true in large bandgap semiconductors and insulators. Thus it is important to ascertain a number of characteristic physical surface parameters of such materials in order to better correlate experimental measurements with theoretical models.

For studying catalysts, physical chemists have developed techniques of determining surface areas and local geometry by means of gas adsorption (Young, 1962). Typically the amount of gas adsorbed on a surface is measured as a function of pressure at constant temperature. In 1938 Brunauer, Emmett and Teller succeeded in deriving an equation which usually fits experimental adsorption isotherm data over a relative pressure range of about 0.05 to 0.35, the relative pressure being defined as the actual gas pressure divided by its vapor pressure at the measurement temperature. This equation is relatively simple and contains two constants, one of which is closely related to the surface area of the sample. In linear form it becomes:

$$(p/p_0)/[v(1-p/p_0)] = 1/(v_m c) + (c-1/v_m c)\ (p,/p_0)$$

where v_m is the monolayer volume, p/p_0 the relative pressure, v the volume of gas adsorbed, and c a constant related to the adsorption binding energy among other factors.

If the volume of gas adsorbed is measured in units of cm^3 at S.T.P., then the surface area in m^2 is taken to be 4.38 v_m when nitrogen is used as the adsorbate gas. Thus, one needs only to fit experimental data to this equation in order to evaluate a surface area which is termed the "B.E.T. area" and has achieved wide acceptance as a characteristic parameter in surface studies.

At higher pressures the adsorption may be affected by the presence of small pores or capillaries in a porous solid resulting in hysteresis which appears when the adsorption and desorption isotherms are compared. DeBoer (1958) and others have developed models which make it possible to evaluate the size and number distribution of these pores from an analysis of the complete adsorption-desorption isotherm.

The work reported here used a gas burette connected to a manometer and to a sample which was held at 78 K. Fig. 1 is a semi-scale drawing of the complete adsorption apparatus. A known amount of nitrogen gas was allowed to come into contact with the sample and the pressure of the system measured. By knowing the volume of the system it was possible to determine the amount of gas remaining in the gas phase and the difference between these two amounts was taken as the volume of gas adsorbed. Suitable alteration of the volume and the amount of gas in the system made it possible to determine the volume of gas adsorbed as a function of pressure. More details on the experimental method pertaining to the actual apparatus used are given by Rutledge (1966). The data were then plotted as v vs. p/p_0 to give an adsorption isotherm. In addition $(p/p_0)/[v(1-p/p_0)]$ vs. p/p_0 was plotted in accordance with the

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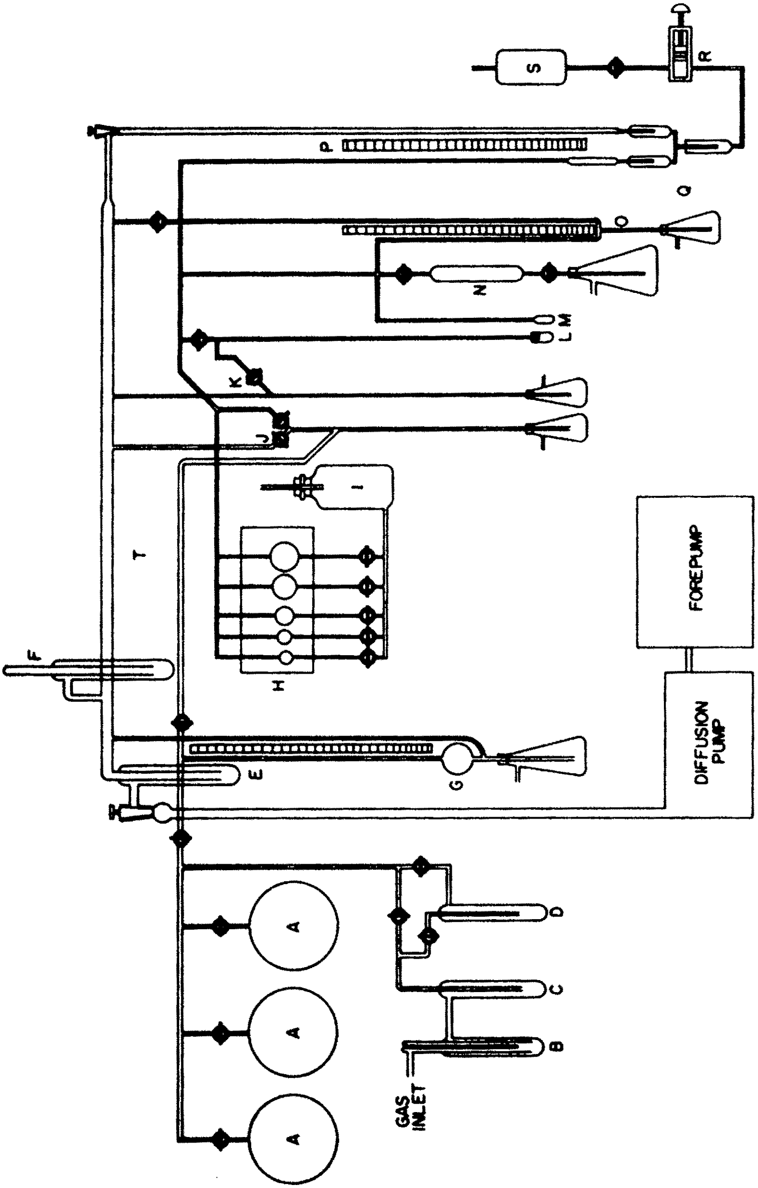

Fig. 1. Gas adsorption apparatus

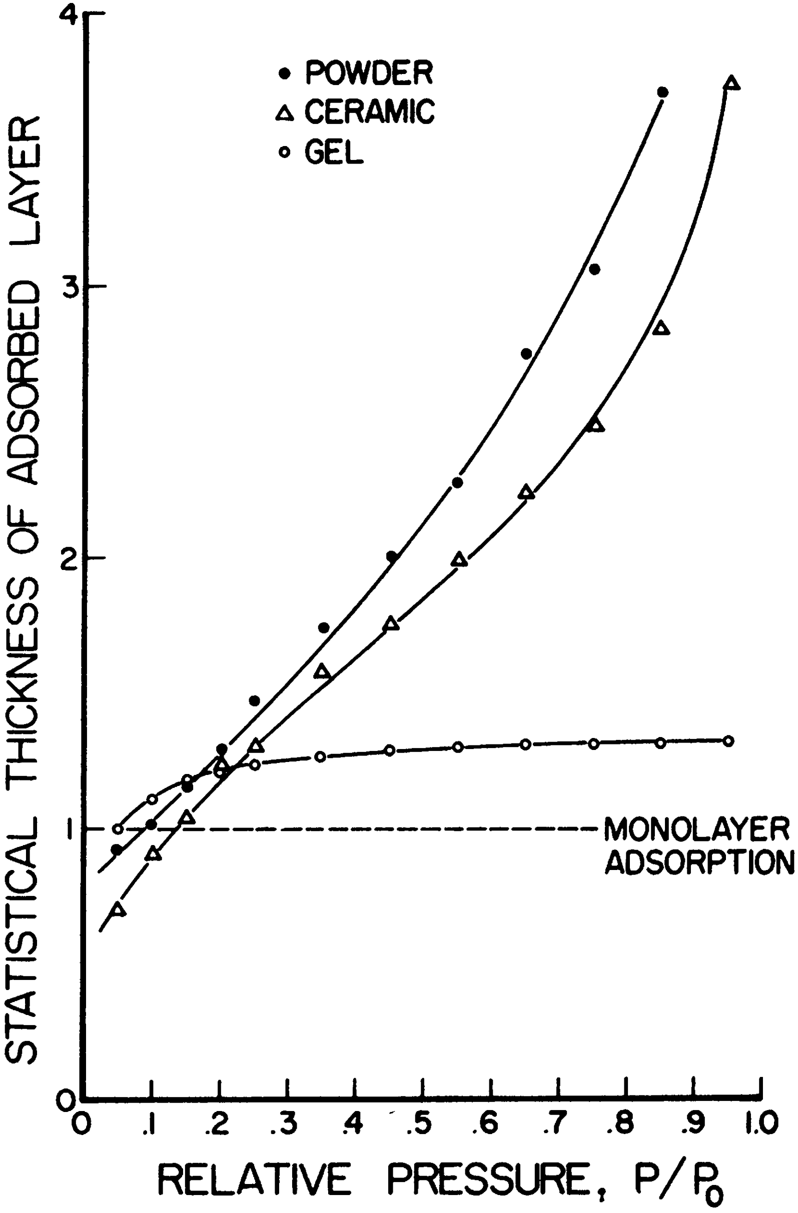

Fig. 2. **Statistical thickness of adsorbed layers**

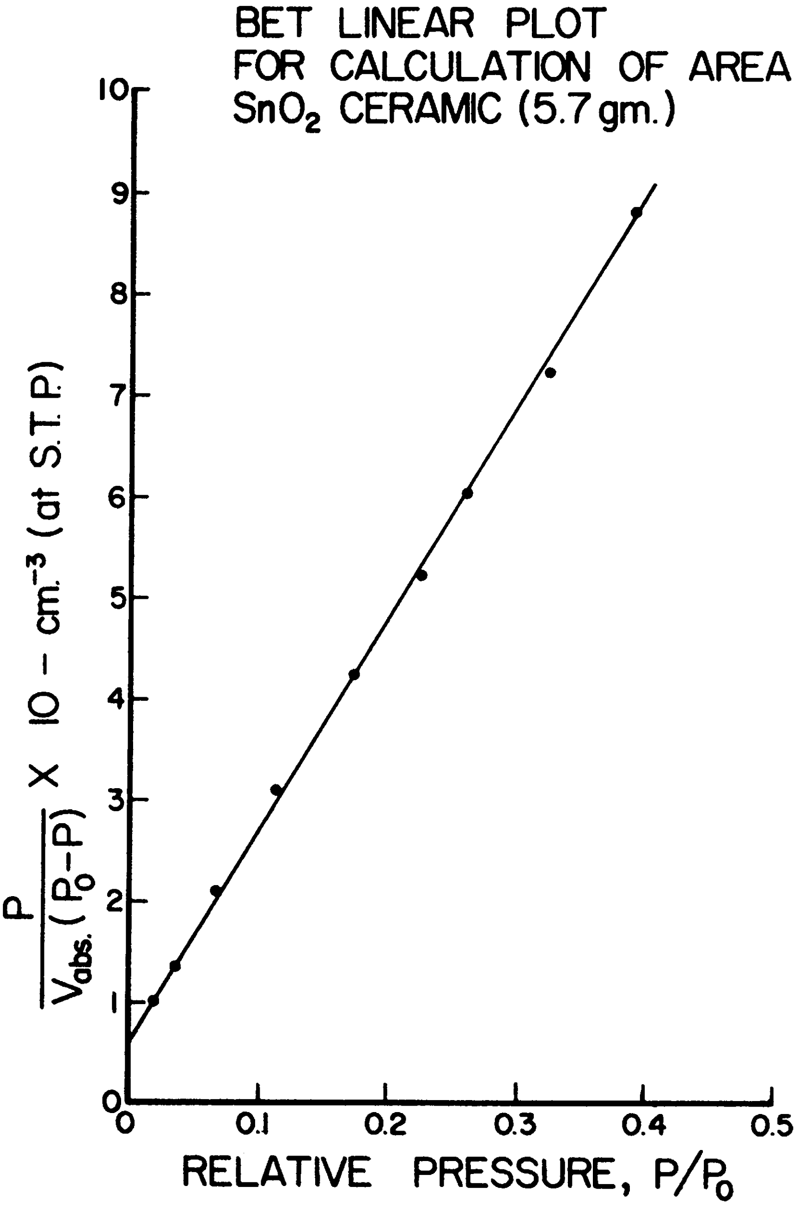

Fig. 3. Linear B.E.T. plot for ceramic sample

linear form of the B.E.T. equation and the area calculated.

This series of measurements was taken on three forms of stannic oxide: powder, ceramic and gel. Fig. 2 is a plot of statistical thickness (v/v_m) in order to remove the area factor from the isotherms for comparison purposes. In each case this plot is proportional to the adsorption isotherm though the constant of proportionality varies with each curve. Fig. 3 is a representative B.E.T. plot, in this instance for the ceramic sample.

The adsorption isotherm exhibited by the powder sample is Brunauer's type II with no hysteresis. This is taken as evidence that pore or capillary effects are nonexistent. Evaluation of the B.E.T. plot yielded a surface area of 2 m^2/g. This area used with a spherical-particle model to calculate the effective particle diameter yielded a value of 0.5 μ, which agrees well with the microscopically evaluated average diameter of 1.5 μ. Thus, one concludes that the powder may be characterized by small nonporous grains.

The adsorption isotherm exhibited by the ceramic was also type II with no hysteresis. This may be taken to imply that only a negligible number of pores with radii less than 300 A were present. A spherical-pore model similar to the one for the powder gave a pore diameter of 5000 A (0.5 μ) which is consistent with the lack of hysteresis above noted. The B.E.T. area was determined to be 0.37 m^2/g.

The gel, as is normally expected of such materials, exhibited a large B.E.T. area, 173 m^2/g, in excellent agreement with Goodman and Gregg's (1960) value of 172 m^2/g. In addition the associated isotherm is type I without hysteresis which is taken to indicate capillary condensation in very fine capillaries, i.e., pores of molecular dimensions.

Further work in this study will include oxygen chemisorption on these surfaces in order to correlate oxygen adsorption to electrical properties. It should be possible by varying the preparation of the ceramic samples, giving different surface areas, to determine which electronic states may be associated with the surface. In addition, the gel, since it is characterized by a large surface area, will be a suitable base for adsorbing gases in order to determine binding properties using infrared and nuclear magnetic resonance measurements.

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