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POSSIBILITIES OF THE CHARACTERIZATION OF SOLIDS BY ESTIMATION OF THEIR SURFACE ACTIVITY AND DEFECT STATE BY EMANATION THERMAL ANALYSIS AND BY SURFACE AREA MEASUREMENTS

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ABSTRACT

The possibilities of the estimation of the surface activity of dispersed solids by gas adsorption surface area measurements and by ETA are compared.

In practice, it is often necessary to estimate the reactivity of a solid substance in its interaction with the surrounding medium. In a series of samples with the same character of the phase boundary (i.e. of the surface of the solid in question) this reactivity is supposed to be proportional to the surface area. Real solid substances represent often systems consisting of small particles (aggregates) with an uneven surface containing pores of various forms and sizes, so that their total surface cannot be determined by geometrical (even microscopical) measurements. The surface area of the solid has therefore to be determined indirectly by measuring its interaction (usually physical adsorption) with a suitable fluid (gaseous or liquid) phase.

The aim of all adsorption methods is to determine the amount of adsorbate molecules needed for the formation of a completed monolayer on the solid phase surface. The specific surface area (usually in m^2 per gram of the solid) is then obtained by multiplying the number of the adsorbate molecules by the efficient area σ of one molecule.

Adsorption measurements are mostly performed by determining the adsorbed quantity x of the gaseous phase as a function of its equilibrium pressure p at a constant temperature T. The adsorption isotherm is usually represented by plotting x/x_m against p/p_o (where x_m is the supposed monolayer capacity and p_o the pressure of the saturated vapours of the adsorbate at the temperature T of the measurement). The specific area S may be calculated from x_m (in cm^3 (NTP) of the adsorbate per gram of the adsorbent) using the formula

$$S = \frac{x_m}{22414} N_o \sigma \times 10^{-20} \qquad (1)$$

where N_o is Avogadro's constant 6.023×10^{23} molecules per mole.

The difficulty in the evaluation of these measurements consists in the determination of the point on the adsorption isotherm corresponding to $x/x_m = 1$, i.e. to the formation of the completed adsorbate monolayer. Besides the earliest method of the inflexion point B (which, however, is not formed on all types of

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adsorption isotherms) a number of isotherm equations has been suggested (Tab.1).

Table 1: Equations of Adsorption Isotherms

Equation	Note
Brunauer, Emmett, Teller (BET) /1/ $\frac{p}{x(p_o - p)} = \frac{1}{x_m c} + \frac{c-1}{x_m c} \cdot \frac{p}{p_o}$	constant c introduced, postulated linear relation between $\frac{p}{x(p_o - p)}$ and $\frac{p}{p_o}$
Anderson, Brunauer /2,3/ $\frac{k \cdot p}{x(p_o - p)} = \frac{1}{x_m c} + \frac{c-1}{x_m c} \cdot \frac{k \cdot p}{p_o}$	further constant k introduced
Frenkel, Halsey, Hill (FHH) /4/ $\ln \frac{p}{p_o} = -b \left(\frac{x}{x_m}\right)^s$	empirical constants b and s ($\doteq 2$) introduced, logarithmic plot
Dubinin, Radushkevich (D-R) /5/ $\ln \frac{x}{V_p \varrho} = -D \left(RT \ln \frac{p_o}{p}\right)^2$	V_p total volume of micropores ϱ density of the adsorbate in liquid state D constant characterizing the Gaussian distribution
Kaganer /6/ $\ln \frac{x}{x_m} = -D \left(RT \ln \frac{p_o}{p}\right)^2$	substitution of the term $V_p \varrho$ by x_m

In spite of the different ways of the evaluation of adsorption measurements by individual authors and the resulting somewhat differing numerical values of the specific surface areas these values represent, especially when obtained with the BET method, data generally considered as standardized.

However, we have to keep in mind that both the temperature and pressure range of adsorption measurements are very limited and situated well below the temperatures and pressures at which the interactions we are interested in take place and at which therefore the reactivity of the solid phase should be determined.

On the contrary, emanation thermal analysis (ETA) /7/ based on the measurement of the release of the radioactive inert gases from previously labelled solids may be used in a practically unlimited range of pressures and at all temperatures above the boiling point of the inert gas in question. It allows us also to perform dynamic measurements, indicating rapid time changes of the reactivity of the solid phase (including not only the surface area but also the morphology, especially the microporous structure, and the defect state of the surface).

The total emanation rate (emanation capacity) E represents a sum of three terms corresponding to the individual mechanisms:

$$E = E_R + E_P + E_S \,.$$

The character of the individual terms is presented in Table 2.

Table 2: Terms of the Total Emanation Rate E

	TERM		
	E_R	E_P	E_S
Mechanism	Recoil of Rn atoms formed from Th and/or Ra	Diffusion through the open pores	Diffusion through the matrix of the solid
Dependence on temperature and surface area	$E_R \sim S_1$ independent of T	$E_P \sim T^{0.5} S_2$ (macro- and mesopores) $E_P \sim T^{-1} S_2$ (micropores)	$E_S \sim T^{-1} S_3$
Concerned surface area	External surface of the aggregates	Internal surface (total surface of open pores)	Sum of the cross-sections of the Rn diffusion-paths in both external and internal surface

At room temperature the term E_S is negligible: diffusion through the matrix of the solid starts to play an important role only at temperatures of about 0.3 T_m to 0.5 T_m (where T_m is the melting point of the solid). Therefore at e.g. 25 °C it holds that

$$E_{25\,°C} = E_R + E_{P(25\,°C)}, \quad \text{i.e.} \quad E_{25\,°C} = (k_1 \times S_1) + (k_{2(25\,°C)} \times S_2) \,. \tag{2}$$

Both constants depend on the type of the solid and its morphology, k_2 besides that also on temperature - e.g. for a series of ThO_2 samples the approximate relation $k_2 = 1.3 \times 10^{-9}\, T^3$ was found /8/. Supposing that the external geometrical surface S_1 of the aggregates is negligible in comparison with their internal surface S_2, we may consider S_2 equal to S_{ads} (from adsorption measurements) so that

$$E_{25\,°C} = E_R + (k_{2(25\,°C)} \times S_{ads}) \,. \tag{3}$$

The constant k_2 varies not only with the chemical character of the solid but also with the way of its preparation causing differences in the defect state and therefore also in the reactivity of the solids. Thus for a NiO sample prepared from carbonate $k_2(25\,^{\circ}C)$ was 0.36, whereas the same oxide prepared from carbonate exhibited $k_2(25\,^{\circ}C) = 0.27$ /9/.

In contrast to the relationship $E_{25\,^{\circ}C} \sim S_{ads}$ originally accepted by some authors /9,10/ the equation with the constant E_R in better agreement with the adsorption measurements especially with samples with S in the range of 0.1 to 5 m^2 (e.g. Fe_2O_3, ThO_2) /11/. The proportionality between $E_{25\,^{\circ}C}$ and S_{ads} was observed only on samples (e.g. ThO_2, NiO, MgO, ZrO_2) with S in the range of 100 – 300 m^2/g, where $E_R \ll k_2 S_2$ /10/.

For the estimation of S_2 at higher temperatures where the term E_P or even E_S plays a greater role, the difference $\Delta E = E_{P(T)} - E_{P(25\,^{\circ}C)}$, which is proportional to S_2, was introduced. For a sample of ThO_2 a linear relationship between ΔE and S_{ads} for S_{ads} ranging from 0.2 to 20 m^2/g at T up to 1100 °C was found. By this method, points on the time or temperature axis corresponding to surface area changes (including those indicating the initial stages of sintering) can be determined advantageously.

We wish to point out that the investigations in the reactivity of solids (especially oxides, sulphides and other materials employed as catalysts, pigments, ceramic raw materials etc.) should not be limited to adsorption measurements but that they should include also the ETA which gives the possibility of studying these materials directly in the atmosphere and at the temperature of their practical application.

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