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CORRELATION BETWEEN SURFACE AREA AND EMANATION POWER OF SOLIDS

K. HABERSBERGER

J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Máchova 7, 121 38 Prague 2 (Czechoslovakia)

V. BALEK

Nuclear Research Institute, 250 68 Řež (Czechoslovakia)

ABSTRACT

In this discussion contribution to the ICTA workshop on less common methods of thermal analysis, the correlation between ETA results and surface area is discussed.

In the course of this workshop, it was shown that emanation thermal analysis (ETA) represents a useful tool for the investigation of the defect state, texture and reactivity of solids and also their changes, especially during their heating, e.g., during various technological processes. Although normally the ETA curves are either compared with those of standard samples or evaluated in a specific way [1] emanation measurements may also lead to results that are more easily comparable both in magnitude and in a physical sense to data obtained by some other, more traditional technique.

Among the physico-chemical parameters that characterize a solid sample from the point of view of its ability to interact with the surrounding milieu, the specific surface area is probably the most important and most commonly used. This parameter is usually determined by the physical adsorption of non-reactive gases at low pressures and temperatures. The surface area is then calculated from the adsorption isotherm of the solid, i.e., from the amount of the gaseous phase adsorbed as function of its equilibrium pressure, p, at a constant temperature T. In order to avoid time-consuming operations (for the construction of an isotherm in some instances a considerable number of individual measurements may be needed), a dynamic single-point method was suggested in which the adsorbed and desorbed amount of the gas (e.g., nitrogen) is determined at only one pressure p. This amount of

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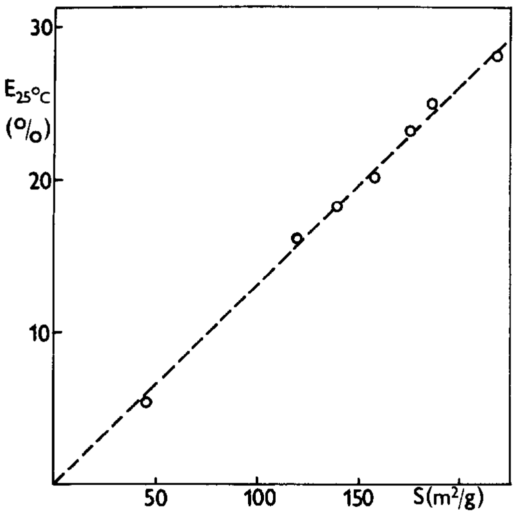

Fig. 1. Emanation rate at room temperature, $E_{25°C}$, determined for a series of MgO samples as function of their specific surface area, S. — — —, Course of the function calculated according to eqn. (1).

adsorbate quantity is then considered to be proportional to the surface area of the sample [2]. For each series of comparable samples the method needs only to be calibrated by means of one standard sample, the surface area of which has been determined by the more orthodox method from the adsorption isotherm.

In spite of the fact that values obtained by adsorption measurements and especially those evaluated according to the BET procedure [3] are generally accepted as standardized, they are far from being absolute, as they depend both on the postulated efficient area of the adsorbate molecule and on the suggested form of the isotherm equation [4]. Hence it is reasonable to use also methods other than adsorption measurements and to employ techniques that have to be calibrated by means of standard samples.

The direct proportionality between the emanation rate measured at room temperature, $E_{25°C}$, and the specific surface area, S, of a series of oxide samples has been postulated previously [5,6] in the form

$$E_{25°C} = k'S \tag{1}$$

By calculating the constant k' from the data obtained by other authors [6], we found for a series of MgO samples with specific surface areas ranging from 42.7 to 217.3 $m^2\ g^{-1}$ a mean value of $k' = 0.131 \pm 0.005$ (standard deviation), i.e., a good proportionality between $E_{25°C}$ and S (Fig. 1).

However, when calculating this dependence of $E_{25°C}$ on S, e.g., for a series of NiO samples prepared from nickel carbonate [7], the equation $E_{25°C} = 0.37S$ gave a worse agreement with the experimental data than the

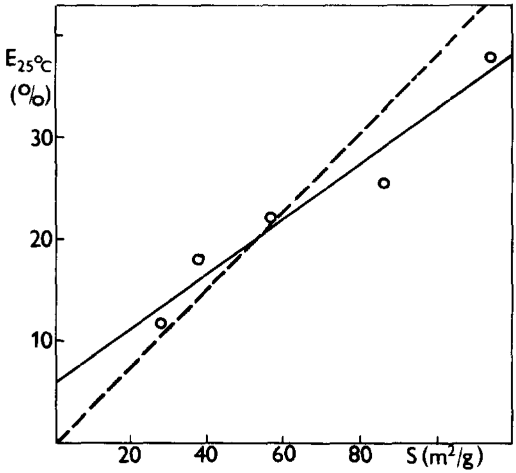

Fig. 2. Emanation rate at room temperature, $E_{25°C}$, determined for a series of NiO samples prepared by thermal decomposition of $Ni(OH)_2$ as function of their specific surface area, S. — — —, Course of the function calculated according to eqn. (1); ———, course of the function calculated according to eqn. (2).

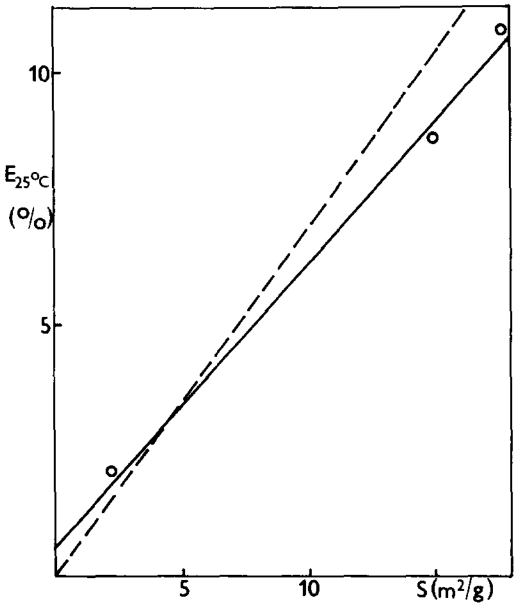

Fig. 3. Emanation rate at room temperature, $E_{25°C}$, determined for a series of ThO_2 samples as function of their specific surface area, S. — — —, Course of the function calculated according to eqn. (1); ———, course of the function calculated according to eqn. (2).

relationship $E_{25°C} = 0.13 + 0.36S$, which was obtained by the least-squares method. With other series of samples the necessity for an equation containing an additive term instead of a simple proportionality (eqn. 1) is still more evident, as, e.g., for a series of other NiO samples (prepared from nickel hydroxide) [7] (Fig. 2) and for a group of ThO_2 samples [8] (Fig. 3). Therefore, a generally valid equation should be

$$E_{25°C} = E_R + kS \tag{2}$$

where the additive term E_R is the partial emanation rate caused by the recoil of Rn atoms formed from Th and/or Ra incorporated in the sample and S is the internal surface area of the solid (i.e., the total surface of its open pores), which in porous solids is much higher than the external surface area of the aggregates and may be considered to be approximately equal to the surface area determined by adsorption measurements [4].

In spite of the fact that with such a relationship two standard samples (with S as different as possible) should be used for calibration, the emanation measurements have the following advantages over adsorption measurements: quick dynamic performance (as with the Nelsen–Eggertsen technique [2]), and the possibility of measuring at room temperature (or even at higher temperatures where the diffusion of Rn through the matrix of the solid is still negligible) and at almost every attainable pressure, whereas both the temperatures and pressures at which adsorption measurements are performed are considerably below those where the reactivity of the solid phase should be investigated. Another advantage of emanation thermal analysis is its ability to follow continuously the changes in the specific surface area of a sample under either stable or varying experimental conditions (pressure, temperature, gas atmosphere, thermochemical treatment, irradiation, etc.).

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