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THERMAL BEHAVIOUR OF SILICAGEL INVESTIGATED BY EMANATION THERMAL ANALYSIS

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ABSTRACT

The thermal behaviour of two different silicagel samples (PORASIL A, S = 300 $m^2 g^{-1}$, Waters, U.S.A., and PRAGOSIL, S = 600 $m^2 g^{-1}$, Nuclear Research Institute, Czechoslovakia) have been characterized by means of the emanation thermal analysis during heating in air at the constant heating rate. The temperature interval of the silicagel stability (950 – 1000 °C corresponds to the relaxation of the silicagel) was established.

INTRODUCTION

Silicagel is one of the most important adsorbents used both in industry and everyday life of people. Its adsorbing properties depend on the surface area, the total volume of pores, the distribution of pores and their accessibility for the adsorbed agent. As numerous applications of silicagel take place at elevated temperature it is of interest to investigate its behaviour during heating under these conditions and to ascertain its thermal stability.

In this paper emanation thermal analysis (ref. 1, 2) based on the measurement of the radioactive inert gas release from the previously labelled solids, has been used to investigate the changes taking place in silicagel samples during heating in air. The ETA results are interpreted in agreement with the recent theories of the inert gas diffusion in porous solids, and compared with the results of surface area and porosity measurements.

EXPERIMENTAL

Two silicagel samples were studied: PORASIL A (S = 300 m^2/g, Waters, U.S.A.) and PRAGOSIL (S = 600 m^2/g, Nuclear Research Institute, Czechoslovakia). Radioactive labelling of the samples was made by the impregnation with an aqueous solution containing trace amounts of ^{228}Th and ^{224}Ra as the radioactive parent of ^{220}Rn (Ref. 1).

The labelled samples of the amount of 0.3 g were investigated in the ETA apparatus (Ref. 3) under following conditions: heating rate 10 °C/min, gas medium - air of the flow rate of 50 cm^3/min.

The surface area of the samples was measured by the BET method, the total porosity was measured by the Hg-porosimeter.

The results of the ETA measurements are expressed as the rate of radon release from the sample in the dependence of temperature.

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RESULTS AND DISCUSSION

To describe the thermal behaviour of the samples on the basis of the ETA measurements the following considerations should be taken into account.

Every spherical particle of the silicagel sample represents a disperse medium which can be described (Ref. 4) as composed of small spheres of the diameter of 8 – 20 nm and the pores of the mean diameter of 10 nm (for the scheme of the silicagel morphology see Fig. 1). These spheres can be considered as composed of a large number of smaller spheres of a diameter of approx. 1.5 nm and micropores of the mean diameter of 1.5 nm.

Hence the rate of the radon release measured by the ETA during the non-isothermal heating of the silicagel samples is due to several mechanisms:
(i) Mechanism of the diffusion in pores which takes place at temperatures up to approximately $0.3 - 0.5\ T_m$, where T_m is the melting point of the substance in absolute scale. The coefficient of the radon diffusion in pores can be expressed in the temperature dependence as
$(D_p)_1 \sim f(1/T)$ for micropores, $(D_p)_2 \sim f(T^{1/2})$ for meso- and macropores.
(ii) Mechanism of the volume diffusion which takes place during the heating of silicagel samples over 800 °C where Rn diffusion in the solid matrix occurs. The temperature dependence of the diffusion coefficient of radon in the matrix can be written as $D_s \sim f(1/T)$.
(iii) Mechanism of the radon recoil release which is temperature independent.

The rate of the radon release E from the porous silicagel sample can be expressed by the general relationship

$$E = f\left[(D_p)_1, (D_p)_2, D_s, x_1, x_2, S_1, S_2\right] \qquad (1)$$

where $(D_p)_1$, $(D_p)_2$ and D_s are the respective diffusion coefficientes of radon, x_1 and x_2 are the portions of micropores and macropores, resp., accessible for the radon atoms, S_1 and S_2 are the external and internal surface areas, including the surface area of the open pores, resp.

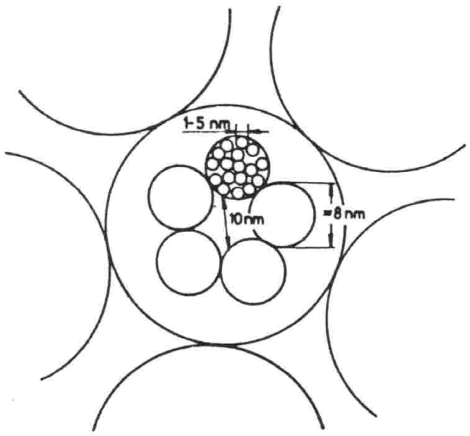

Fig. 1. Scheme of the silicagel morphology

On the basis of these considerations the thermal behaviour of silicagel samples can be evaluated from the results given in Fig. 2.

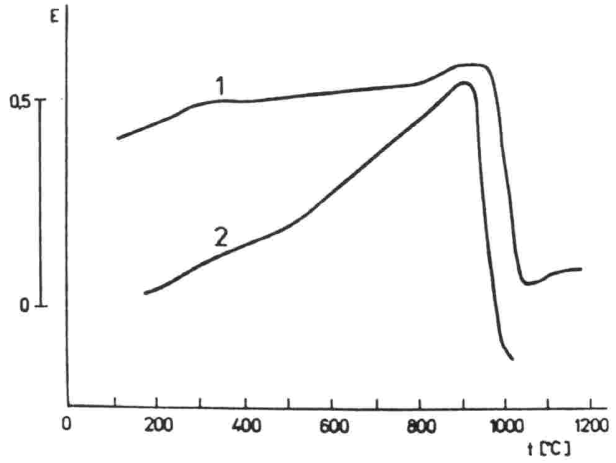

Fig. 2. ETA curves of silicagel samples
PRAGOSIL (curve 1) and PORASIL A (curve 2)

In the temperature range 100 – 300 °C the porous system of silicagel is stable, the diffusion coefficients of radon diffusion in micropores $(D_p)_1$ as well as that in mesopores $(D_p)_2$ can be evaluated from the results in Fig. 2.

Experimentally, the effective coefficient D_{eff} of radon diffusion can be obtained, which is related to the values $(D_p)_1$ and $(D_p)_2$ by the relationship

$$D_{eff} = \frac{(D_p)_1 x_1 + K (D_p)_2 x_2}{x_1 + K x_2} \qquad (2)$$

where $(D_p)_1$, $(D_p)_2$, x_1 and x_2 are the same parameters as in Eq.1, and K - is the equilibrium constant of Rn migration between the micro- and mesopores.

The enhanced radon release rate at the temperatures above 500 °C (see Fig. 2, curve 2) is due to the increase of the fraction of micropores x_1 open to Rn diffusion as a consequence of the release of hydroxyl water. The parameter x_1 can be evaluated from the temperature dependence of the radon release rate in Fig. 2. This process is accompanied by the increase of the surface area (Ref. 5). The limit of the thermal stability of silicagel is 950 – 1000 °C; during heating to higher temperatures the silicagel porous system collapses, which is expressed by the decrease of the surface area of the sample (for the sample heated to 1000 °C S = 2.4 $m^2 g^{-1}$)and the decrease of the total volume of pores. The abrupt falling down of the radon release rate in this temperature range indicates the closure of the diffusion pathes via open pores. This effect is stressed by the fact that the parent nuclides of Rn penetrate into the deeper layers of the sample.

At temperatures above 1000 °C the volume diffusion mechanism of the radon release takes place which is indicated by the increase of the radon release rate.

The comparison of the behaviours of two silicagel samples studied can be made, using the ETA curves in Fig. 2. Differences in the morphology (surface area) of the samples are reflected by the radon release rate E at room temperature: higher E values correspond to the sample PRAGOSIL possessing a relatively larger surface area. It is interesting to note that the dehydroxylation is not expressed by the increase of E with the sample; we suppose that the portion x_1 of the opened pores is high enough in the starting material before the thermal treatment so that no increase of x_1 is to be observed.

The values $(D_p)_1$ and $(D_p)_2$ evaluated from the ETA curves in Fig. 2 differ for the samples PORASIL and PRAGOSIL: the higher value corresponds to the former one. The thermal stability of the PORASIL sample is slightly lower than that of PRAGOSIL.

It should be mentioned here that the theoretical ETA curve for silicagel sample simulating the thermal behaviour of PRAGOSIL has been derived by means of a computer modelling (Ref. 6). The result fits well with the ETA curve experimentally found in this paper.

The coefficient of radon diffusion in the relaxed silica matrix has been evaluated from the upper part of the ETA curve 1 in Fig. 2.

CONCLUSION

The emanation thermal analysis enabled us to yield complementary data about the thermal behaviour of silicagel during the non-isothermal treatment. The thermal stability of silicagel samples was assessed and the characterization of the silicagel porous system and of the silica matrix have been made by means of the ETA. The model of silicagel structure as a two-sized pore system has been applied to the description of the thermal behaviours of the samples studied.

The ETA can be recommended for the characterization of other highly porous solids, mainly containing micropores. This method is especially sensitive to the changes in the microporosity, as the pore size of the micropores is comparable with the diameter of Radon atoms (d = 0.4 nm).

By the ETA the characterization of porous solids can be made directly in dynamic conditions of heating, without the necessity of the interruption of the thermal treatment and the cooling the sample, as it is usual with the common absorption methods.

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