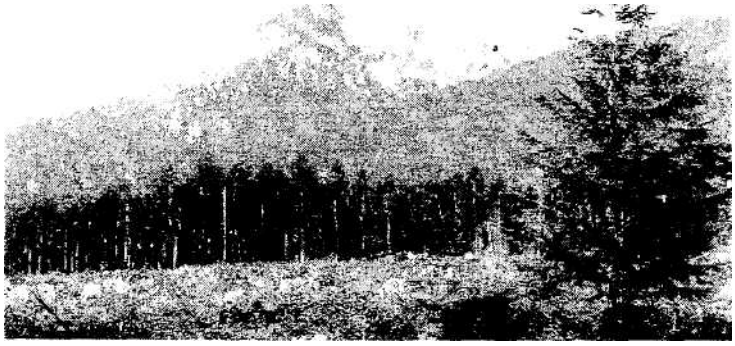

Slovak Group for Thermal Analysis and Calorimetry
Slovak Society of Chemistry
Faculty of Chemical and Food Technology, STU
Slovak Silicate Society

XVII. Conference on Thermal Analysis and Calorimetry
Termanal 2005
Stara Lesna, Slovak Republic High Tatras - Hotel Academia 2-5 October 2005
Plenary lectures, P25-28.

EMANATION THERMAL ANALYSIS IN THE INVESTIGATIONS OF SOLID SURFACES AND SUBSURFACES

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In the recent years emanation thermal analysis (ETA) [1-4] has been used as a tool in the investigation of surfaces and subsurfaces of solids. The emanation thermal analysis consists in the measurement of the release of inert gas (radon) from a solid sample. The release of the inert gas atoms incorporated into the sample makes it possible to monitor changes in morphology, in the roughness of surfaces, and the microstructure of subsurface of solid samples under *in situ* treatment conditions. From the results published in numerous papers and monographs [1-22] it follows that the ETA gave a supplementary insight into the alteration of solid surfaces due to thermal treatment, mechanical treatment, chemical interactions, radiation effects, *etc.* The ETA results frequently complemented results of surface characterization by B.E.T., optical and electron microscopy and other methods.

Labeling of samples for ETA measurements

Recoil energy of alpha-decay was used to introduce radon atoms into solids. Trace amount ot thorium ^{228}Th was deposited on the sample surface and atoms of radon ^{220}Rn formed by a spontaneous alpha-decay of ^{228}Th and ^{224}Ra were introduced into the solid owing to the recoil energy (85 keV per atom). Radon atoms penetrated several tens of nanometers into the sample subsurface; for example in SiO_2 65.4 nm and in TiO_2 60 nm.

Use of radon as diffusion structural probe and evaluation of ETA results

Structure irregularities of solids serve as channels for radon diffusion. Changes in the radon diffusion mechanism taking place during heating may reflect microstructure changes of solids. Supposing that solid state transitions take place in a solid the temperature dependence of emanating power E_{total} can be schematically expressed as

$$E_{TOTAL} = E_R + \Sigma E_{Dn}(T) * \Psi_n(T) \qquad (1)$$

where E_R is the emanating power due to recoil. The emanating power due to radon diffusion is determined by $E_{Dn}(T)$ and $\Psi_n(T)$ functions, characterizing the diffusion and microstructure changes in the respective temperature intervals.

The function $\Psi(T)$ was proposed to describe changes of the number of defects serving as radon diffusion paths [10]. The product $E_D(T)*\Psi(T)$ (see Eq. 1) was used to describe the annealing

of defects, phase changes or other solid state transitions. The function $E_D(T)$ describes the radon diffusion permeability [10]. Eq. 2 was used in modeling temperature dependencies of the emanating power E_D, due to diffusion

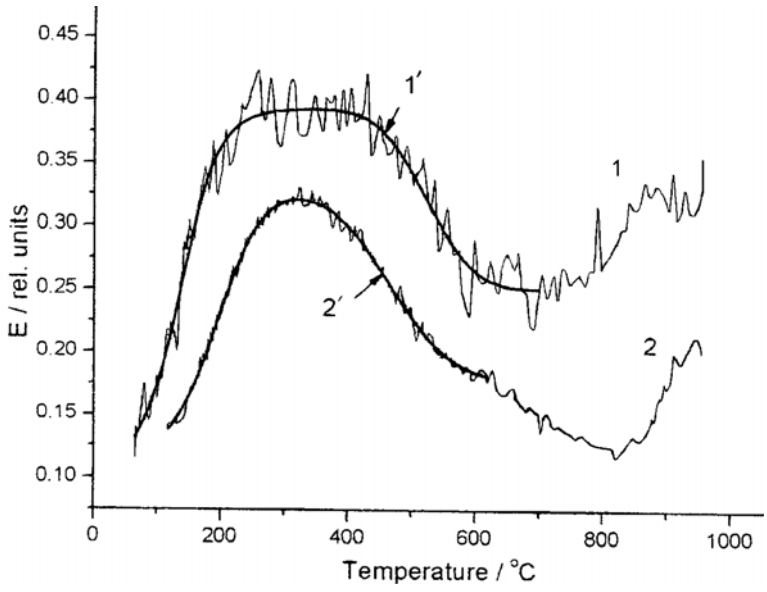
$$E_D = \frac{3}{y}\left(\coth y - \frac{1}{y}\right) \qquad (2)$$

where $y(T) = \frac{S}{M}\frac{\rho}{\sqrt{\frac{D}{\lambda}}}$.

S/M is the surface area of open pores, inter-granular space and of interfaces serving as radon diffusion paths, *p* is density of the sample, $(D/\lambda)^{1/2}$ is average radon diffusion length. *D* is the radon diffusion coefficient and /. is the radon decay constant.

In the case that the number of radon diffusion paths and/or surface area decreases on heating, the Ψ(T) function has a descending character [10]. The descending character of the Ψ(T) function can be expressed by Eq. 3

$$\Psi(T) = 0{,}5\left[1 + erf\frac{1 - \frac{T_m}{T}}{\frac{\Delta T\sqrt{2}}{T}}\right] \qquad (3)$$



where erf is the sign for the integral Gauss function, T_m is the temperature of maximum rate of the annealing of the defects which serve as radon diffusion paths, ΔT is the temperature interval of the respective solid state process.

Fig.1. ETA experimental results of titania films measured on heating in argon (curve 1) and oxygen (curve 2) compared with the model curves characterising the temperature dependencies of radon mobility in the samples when heated in argon (curve 1); and oxygen (curve 2).

ETA applications and evaluation of results

To determine optimum conditions for the preparation of titania based photoactive materials microstructure changes that took place on heating hydrous titania were investigated by ETA [11-14]. Thermal behavior of sol-gel prepared hydrous titania gel films and the annealing of porosity and surface irregularities of the dehydrated titania layers were also characterized by ETA [15]. The temperature of 500 °C was recommended for the preparation of consolidated polycrystalline anatase film to be used as a photocatalyst. The ETA results characterized the microstructure changes of porous titania films under *in situ* heating in argon or oxygen in the range 20-900 °C (see Fig. I). The differences in the thermal behavior of the samples observed on heating were assessed. It was assumed that the increase of the emanating power, *E.* in the temperature range 50-250 °C was due to the radon diffusion along structure irregularities in surface and subsurface layers. The reduced slope of radon release rate observed during the sample heating in oxygen reflected the decreased amount of radon diffusion paths [16]. On further heating the annealing of structure irregularities and porosity of the titania film was characterized by a decrease of the radon release rate. A good agreement of the experimental

ETA data and the results of mathematical modeling was obtained. XRD results confirmed that the titania films heated up to 800 °C both in argon or oxygen preserved the anatase structure. SEM microphotographs confirmed a grain size growth in the anatase films on heating up to 800 °C.

Fig. 2 depicts ETA results of a porous hematite sample (surface area 85 m^2g^{-1}) and its surface area changes. The emanating power, *E,* increased on sample heating from 50°C until 420°C due to radon diffusion. The decrease of E in the range from 420°C to 510°C was ascribed to the annealing of porosity and surface area of the sample [17]. It was demonstrated that the ETA brought about interesting information about changes in surface layered structure of synthetic hydrotalcite like minerals - layered double hydroxides with different composition, like Mg-Fe-CO_3- LDH or Mg-Al-CO_3 LDH [18, 19] as well as synthetic mineral gibbsite [20].

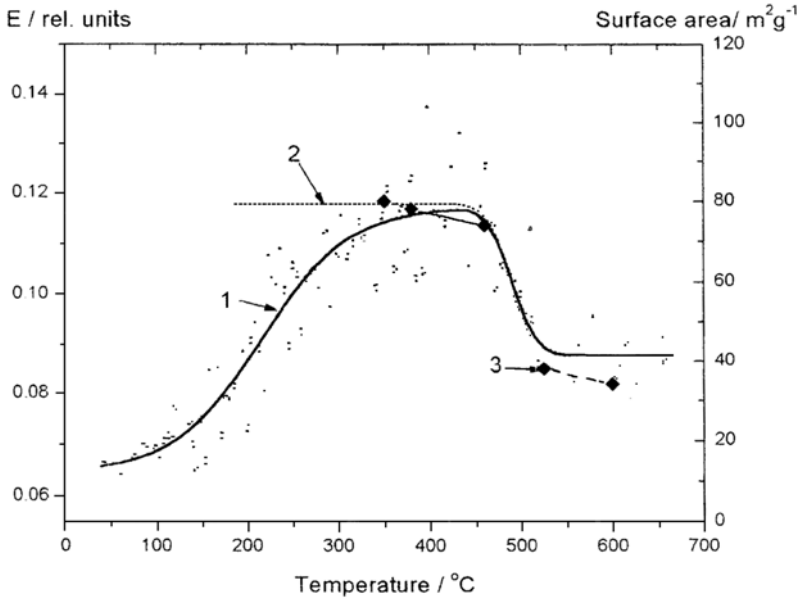


Fig 2. Results of ETA compared with BET surface area that characterize the thermal behavior of porous hematite. Points-experimental ETA data, curve 1-full line - results of ETA modeling by using Eqs. 1 and 2, curve 2- dashed line temperature dependence of Ψ(T) fitted by using Eq. 3, curve 3 - values of B.E. T surface area of hematite sample heated in different temperatures.

Moreover, interesting information was obtained by ETA about changes in the interlaycr spacings that accompanied the dehydration of clay minerals, like vermiculite and Na-montmorillonite saturated with various cations [21, 22].

Conclusions

ETA reflected changes in surface and subsurface irregularities of the solids under *in situ* conditions of the heat treatment. A complementary information to that obtained by DTA, TG, XRD, SEM, surface area and porosity determination by nitrogen adsorption was achieved.

Acknowledgments

This work was supported by the Grant Agency of the Czech Republic (project No. 104/04/0467) and by the Ministry of Education of the Czech Republic (Project No. LA-040).

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