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Study of thermal evolution of porous hematite by emanation thermal analysis

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Abstract

Emanation thermal analysis (ETA) was used for the characterization of surface and porosity annealing of acicular porous hematite samples in the temperature range from 20 to 600 °C under in situ conditions of heating in air flow. Two hematite samples with different surface areas (85 and 44 $m^2\ g^{-1}$, respectively) were prepared by thermal decomposition of goethite using constant rate thermal analysis (CRTA) equipment. ETA results characterizing the thermal evolution of the porous hematite samples were compared with surface area determined by B.E.T. method, transmission electron micrographs and crystallite size determined by XRD.

Keywords: Electron microscopy; Emanation thermal analysis; Fe_2O_3; Porosity

1. Introduction

In order to characterize thermal stability of porous materials by nitrogen adsorption measurements or electron microscopy, samples heated to different temperatures have to be subsequently cooled before their characterization. One disadvantage of this approach is that reversible processes which could eventually take place during heating or cooling of the solids can not be observed. In contrary, emanation thermal analysis (ETA)[1] makes it possible to study the evolution of the porosity and surface area of the samples under in situ conditions of the heating. This method has been already advantageously used for the characterization of various materials, such as nanosized powders, gels, thin films, as well as bulk solids on heating in selected gas environments.[2–6]

ETA[1] is based on the measurement of radon release rate from the samples previously labelled by trace amounts of ^{228}Th and ^{224}Ra radionuclides. Atoms of radon, ^{220}Rn are formed by the spontaneous α-decay of ^{228}Th and ^{224}Ra. The ^{224}Ra and ^{220}Rn atoms can be incorporated into the sample due to the recoil energy (85 keV $atom^{-1}$) which the atoms gained by the α-spontaneous decay. By this way the parent nuclides of ^{228}Th and ^{224}Ra serve as "recoil ion implantators" of the radon atoms.[7]

The mechanisms of radon release from labelled samples are (i) release due to the recoil energy of the radon atoms, (ii) diffusion in open pores and in intergranular space, and (iii) radon diffusion in the matrix of the solids.[1] The radon release rate, E (also called emanating rate), can be written

$$E = E_{\text{recoil}} + E_{\text{pores}} + E_{\text{matrix}} \tag{1}$$

The emanting rate E due to recoil can be expressed as

$$E_{\text{recoil}} = K_1 S_1 \tag{2}$$

where K_1 is a temperature-independent constant, that depends on the path of the recoiled radon atoms in the solid, and S_1 is the external surface area of the sample.

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The emanating rate due to radon diffusion in the intergranular space and open pores, E_{pores}, can be expressed as

$$E_{\mathrm{pores}} = K_2 S_2 \tag{3}$$

where K_2 is a constant which depends on temperature, and S_2 is the internal surface area of the sample including open pores.

The emanating rate due to the radon diffusion in the solid matrix of the sample, E_{matrix}, can be expressed as

$$E_{\mathrm{matrix}} = K_3 S_3 \exp(-\Delta H/2\mathbf{R}T) \tag{4}$$

where K_3 is a temperature-independent constant, ΔH is the activation enthalpy of radon diffusion in the solid matrix, $\mathbf{R}$ is the molar gas constant, T is the absolute temperature and S_3 is the surface area representing the sum of the cross sections of all diffusion paths, such as dislocations, grain boundaries, etc.

Consequently, processes that could be investigated by means of ETA are those accompanied by changes of surface area and/or microstructure of the solid samples, affecting the radon release from the solids.

In this study, two samples of porous hematite prepared by thermal decomposition of goethite under constant rate thermal conditions were characterized by means of ETA. Results of ETA were compared with the surface area measurements, electron micrographs as well as crystallite size determined by X-ray diffraction.

2. Experimental

2.1. Preparation of porous hematite

The hematite samples with surface area 85 and 44 m^2 g^{-1}, respectively were prepared by thermal decomposition of goethite.[8] using constant rate thermal analysis (CRTA) equipment. This equipment consisted of a tubular furnace connected to a vacuum system.[9,10] The pressure gauge was interfaced to the temperature controller; thus, the temperature evolution was controlled by the pressure signal in order to maintain the pressure constant along the process. For hematite of surface area 85 m^2 g^{-1} the constant pressure was maintained at the value of 5.5×10^{-5} Torr whereas for the preparation of hematite of surface area 44 m^2 g^{-1} the pressure was maintained at 8 Torr. A more detailed description of the preparation method could be found in Refs.[8,11]

2.2. Characterization methods

The ETA measurements were carried out using a modified DTA-ETA equipment Model NETZSCH 404 (the heating rate was 5 °C min^{-1}, the air flow was 50 ml min^{-1}). During the ETA measurements, the labelled sample of 0.05 g was situated in a corundum crucible immersed in a constant air flow, which carried the radon released from the sample into the measuring chamber of radon radioactivity.

Samples for ETA measurements, were labelled using the adsorption of traces of ^{228}Th and ^{224}Ra on the sample surface from acetone solution. The specific activity of the samples was 10^5 Bq per ml. Samples were stored for three weeks prior to ETA measurements to allow radioactive equilibrium to be reached.[1] The recoiled radon atoms penetrated into the samples due to the recoil energy (85 keV per atom) of ^{224}Ra and ^{220}Rn.

The concentration profiles of ^{224}Ra and ^{220}Rn were calculated by Monte Carlo method and using TRIM code.[12] The calculated values of the recoil ranges in α-Fe_2O_3 (hematite) are: for ^{224}Ra: 26.1 nm (straggling 6.8 nm) and for ^{220}Rn 25.9 nm (straggling 7.3 nm), respectively. Therefore, we consider the penetration depth of ^{220}Rn atoms in the hematite to be up to 66 nm. The high amount of ^{220}Rn was situated next to the surface having the descendent character of the concentration profile from the surface.[7,13]

The ETA results are presented in this study as temperature dependencies of the radon release rate, E, normalized to the total radioactivity of the parent nuclides used for the sample labelling.

Transmission electron microscopy (TEM) examinations were performed with a Philips CM10 microscope. The X-ray diffraction (XRD) patterns were obtained by means of a Siemens equipment model D 5000 using Ni-filtered Cu$K\alpha$ radiation. The dimensions of the coherently diffracting domains (crystallite size) of hematite were determined from the full-width of the half maximum of the (104) and (110) XRD lines using the Scherrer's equation.[14] Surface area measurements were performed by Micromeritics 2000 apparatus and evaluated by using the B.E.T. single point method with N_2 as an absorbate at liquid N_2 temperature.

3. Results and discussion

The ETA results of the porous hematite sample with 85 m^2 g^{-1} are presented in Fig. 1, curve 1. The emanating rate, E, increased on sample heating from 110 to 420 °C. We assumed that the increase was controlled by the radon diffusion along structure irregularities, cracks and pores serving as radon diffusion paths. The decrease of E in the range from 420 to 510 °C was ascribed to the annealing and the structure irregularities of the hematite sample. Taking into account that the thickness of the acicular hematite particles was not larger than 30 nm, we supposed that the sample was labelled by radon atoms in all the volume and the information obtained from the ETA curve is related to the behaviour of all the sample volume.

In order to compare the ETA results of porous hematite with the direct measurements of surface area, TEM characterization of morphology and XRD characterization of crystallite size, several fractions of the porous hematite were heated up to different temperatures from 350 to 600 °C under otherwise identical experimental conditions to those used for ETA (i.e. heating at dry air flow and at the heating rate 5 °C min^{-1}) and quenched to room temperature. Surface area values (S) of the hematite samples heated to various temperatures are presented in Fig. 1, curve 2. It is obvious from curve 2, Fig. 1 that on heating up to 440 °C, the S values of this hematite sample remained unchanged at $\sim$80 $\text{m}^2\ \text{g}^{-1}$, while when the sample was heated to 525 °C the S decrease to 40 $\text{m}^2\ \text{g}^{-1}$ was observed. The surface area of the sample heated to 600 °C was 38 $\text{m}^2\ \text{g}^{-1}$, therefore, it is shown that no further substantial annealing of the porosity took place above 520 °C.

From the TEM micrograph it follows that the "as prepared" porous hematite sample (Fig. 2a), consists of slit shaped pores open along the longest dimension of the particles. It was previously observed that the elongated direction of the crystal is perpendicular to the c axis.[15]

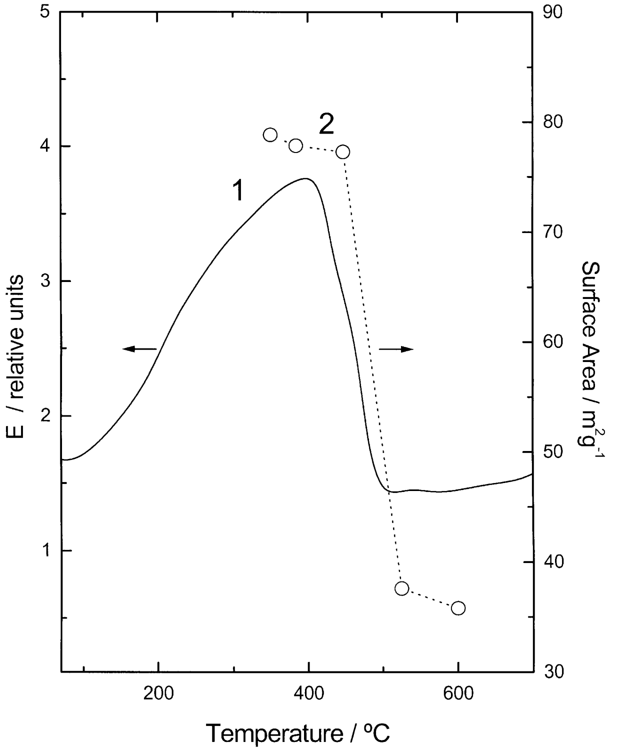

Fig. 1. Temperature dependence of the radon release rate obtained by ETA measurements of hematite surface area 83 $\text{m}^2\ \text{g}^{-1}$ (curve 1) and of the surface area of the samples preheated to the selected temperatures in the range 380–600 °C (curve 2).

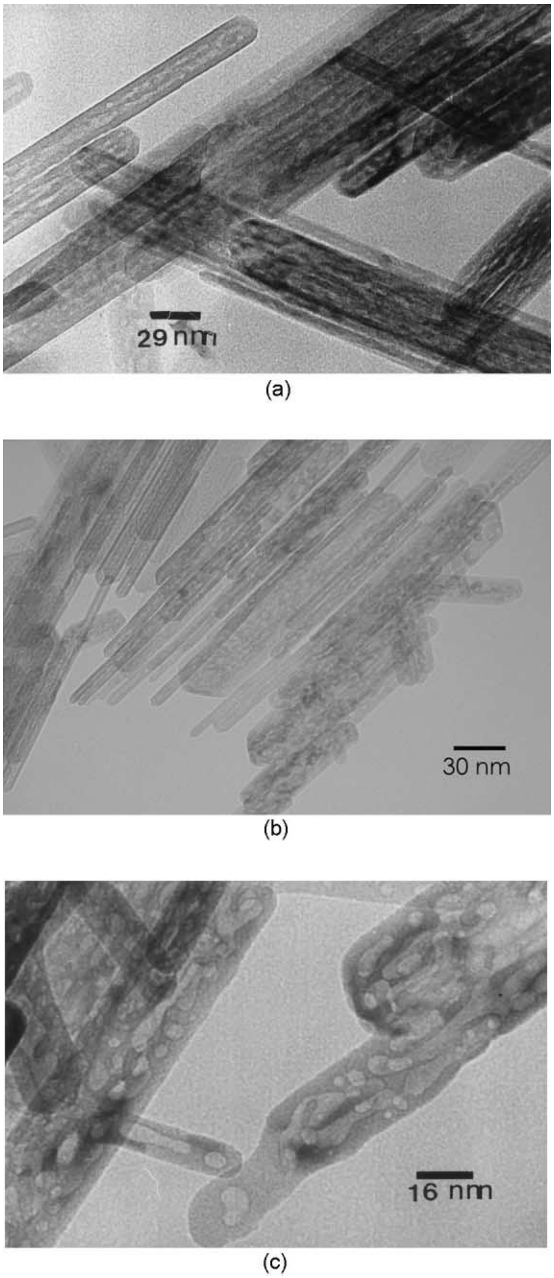

Fig. 2. Transmission electron micrographs of porous hematite sample with surface area 83 $\text{m}^2\ \text{g}^{-1}$ (a) as prepared, (b) heated to 440 °C and (c) heated to 600 °C.

Table 1
Crystallite sizes of hematite heated to different temperatures estimated from the broadening of the XRD (104) and (110) lines

Temperature/°C	Crystallite size	
	d_{104}/(nm)	d_{110}/(nm)
350	10	34
380	10	34
460	10	34
500	13	34
600	14	34

The TEM micrographs of the porous hematite heated to 440 and 600 °C are shown in Fig. 2b and c, respectively. The sample heated at 440 °C, has a similar microstructure to the "as prepared" hematite (see Fig. 2a). In the sample treated at 600 °C, the pores that open along the longest direction disappeared, and isolated cylindrical pores were observed (see Fig. 2c). Particle growth or sintering was not observed by TEM in the samples heated to 440 and 600 °C, respectively. A similar behaviour of porous hematite after heat treatment was already reported by other authors. [16,17]

Moreover, the ETA results were compared with the evolution of the crystallite size of hematite, estimated from the broadening of the XRD (104) and (110) diffraction lines. Table 1 includes the crystallite size values of hematite samples heated to various temperatures from 350 to 600 °C. Taking into consideration that the slit shaped micropores are perpendicular to the c axis, the (110) and (104) lines can give some indication of the dimensions of the crystallite in the directions of the pores and perpendicular to the pores, respectively. It was found that in the (110) direction no changes in the crystallite sizes were observed for the samples heated to the mentioned temperatures. However, in the (104) direction the crystallite size increases for the samples heated to 500 and 600 °C, respectively. These results are consistent with the TEM micrographs demonstrating that the as prepared porous hematite was divided into several parts after the annealing of the pores grow together. Consequently, we can suppose that the ordering of the hematite structure resulted during the annealing of the elongated pores. This is in support of the ETA results indicating the decrease of the defects amount serving as radon diffusion paths just in the temperature preceding 500 °C. For the samples heated at temperatures lower than 460 °C, the crystallite size in the (104) direction remained unchanged. Thus, the ETA results indicating the decrease of E in the range from 420 to 510 °C, reflected the annealing of open porosity which is in agreement with the surface area measurements and crystallite size calculations from XRD data.

The ETA results of porous hematite with a surface area of 44 $m^2\ g^{-1}$ are presented in Fig. 3, curve 1. We assume that the increase of emanating rate, E, in the range from 110 to 600 °C is controlled by the radon diffusion along near surface irregularities, cracks and pores serving as radon diffusion paths. This mechanism was already assumed for the radon release in the above temperature range observed with the hematite sample of the surface area 85 $m^2\ g^{-1}$ (see Fig. 1, curve 1), although

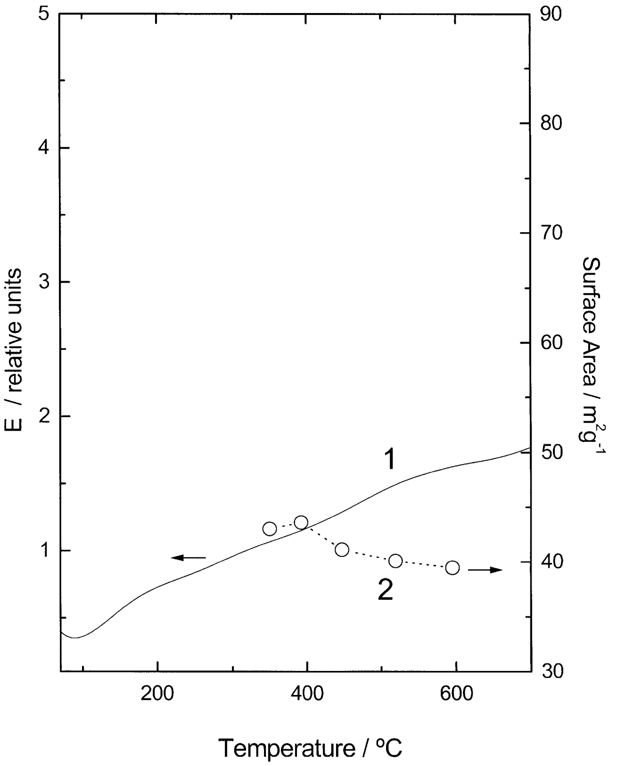

Fig. 3. Temperature dependence of the radon release rate obtained by ETA measurements of hematite surface area 44 $m^2\ g^1$ (curve 1) and of the surface area of the samples preheated to temperatures in the range 380–600 °C (curve 2).

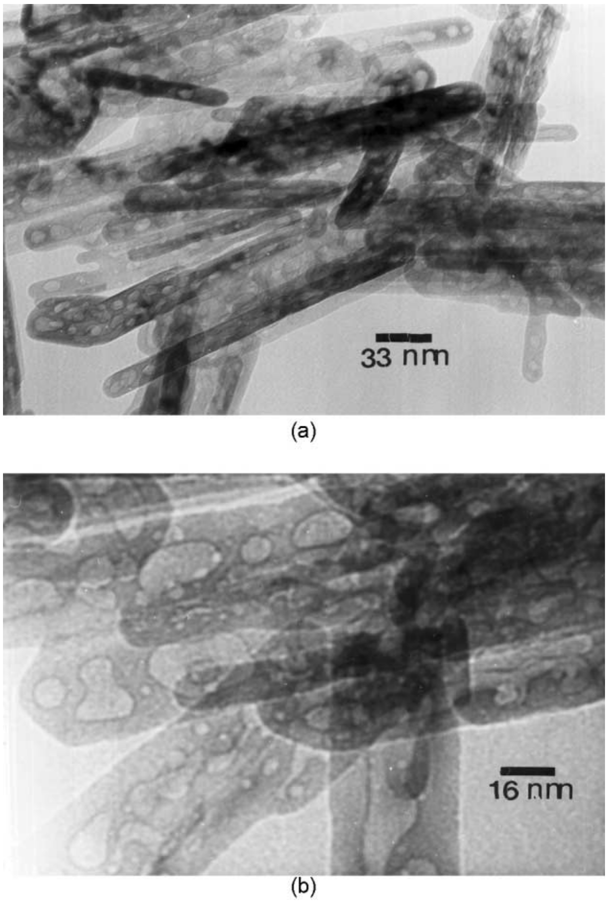

Fig. 4. Transmission electron micrographs of hematite sample with the surface area of 44 $m^2\ g^{-1}$ (a) as prepared, (b) heated to 600 °C.

a more intense increase of E was observed with the sample of higher surface area and porosity, serving as a diffusion channel for radon. In contrast, to the thermal behaviour of the sample characterized by the ETA (curve 1, Fig. 1) no decrease of emanating rate was observed in curve 1, Fig. 3. Consequently, no annealing of the porosity and surface area was supposed to take place in the sample with the surface area 44 $m^2 g^{-1}$ in the respective temperature range. This assumption was confirmed by the values of surface area of the hematite samples prepared from the initial hematite of 44 $m^2 g^{-1}$ by heating to various temperatures in the range 380–600 °C (curve 2, in Fig. 3). The TEM micrographs (Fig. 4) also confirmed our assumption.

4. Conclusions

The ETA results obtained for porous hematite samples under in situ conditions of heating in air are in agreement with the direct measurements of surface area by nitrogen adsorption, morphology changes observed by TEM as well as with the decrease of the structure defects and crystallite size growth indicated by XRD patterns. We observed that the decrease of the amount of the radon diffusion paths due to the annealing of the hematite porosity and increase of crystallite size took place in the narrow temperature range from 420 to 510 °C. The ETA results are in agreement with the direct surface area measurements, TEM micrographs and XRD patterns of the porous hematite heated to different temperatures. The ETA could be recommended for the determination of the early stages of the annealing of the porous samples giving the information about the onset of the annealing process under in situ conditions of the heating.

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