



ELSEVIER

Thermochimica Acta 340–341 (1999) 301–310

thermochimica
acta

www.elsevier.com/locate/tca

Use of emanation thermal analysis for in-situ monitoring of microstructure changes during heating of hydrous titania and titania containing 10% ruthenia

V. Balek^{a,*}, E. Klosová^a, J. Málek^b, J. Šubrt^c, J. Boháček^c, P. Bezdička^c,
A. Watanabe^d, T. Mitsuhashi^d

^aNuclear Research Institute, CZ-25068 Řež, Czech Republic

^bJoint Laboratory of Solid State Chemistry, Academy of Sciences of the Czech Republic and University of Pardubice, Studentská 84, CZ-530 09 Pardubice, Czech Republic

^cInstitute of Inorganic Chemistry AS CR, CZ-25068 Řež, Czech Republic

^dNational Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

Accepted 6 August 1999

Abstract

Results of emanation thermal analysis (ETA) and thermogravimetry (TG) of hydrous titania and titania containing 10% of ruthenia measured during heating in argon from 20°C to 1000°C are presented. The ETA results are interpreted by comparison with the results of traditional methods such as TG, DTA, XRD, TEM, and surface area measurement. A correspondence of the results was found. The ETA made it possible to monitor microstructure changes under in-situ conditions of heat treatment of the samples. From the ETA results measured during cooling of the heated samples to selected temperatures the values of the activation energy of radon diffusion were determined in order to characterise surface annealing and compaction of samples during heating. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Emanation thermal analysis; Thermogravimetry; Nanosized titania; Titania–ruthenia; Microstructure characterisation

1. Introduction

The mixed oxide TiO₂–RuO₂ system has been proposed as an advanced photocatalyst for water decomposition with enhanced efficiency in comparison with pure TiO₂ [1,2]. It was found [3] that the presence of RuO₂ has a positive electronic effect upon the TiO₂ photocatalyst. This system can also be effectively used for other catalytic reactions of technolo-

gical and environmental importance [4–6]. Although in the first experimental work only a ground mixture of the TiO₂ with RuO₂ was used, intimate contact of both oxides to enhance the positive electronic effect is recommended.

In the National Institute for Research in Inorganic Materials, Tsukuba the TiO₂–RuO₂ system has been studied, aiming to design an effective photocatalyst where the photocatalytical reaction would continue for an extended time period.

The mixed oxide samples were prepared by the hydrolysis of solutions containing ruthenium chloride and titanium chloride and subsequent drying the pre-

*Corresponding author. Tel.: +420-2-2094-1169; fax: +420-2-2094-0567.

E-mail address: bal@nri.cz (V. Balek)

cipitates. In this paper we present results of emanation thermal analysis (ETA) of the in-situ investigation of microstructure changes during heating of the hydrous TiO_2 and hydrous TiO_2 containing 10% of RuO_2 . This investigation was carried out in order to determine optimal conditions for the preparation of catalysts.

2. Experimental

2.1. Preparation of samples

Reagent grade TiCl_4 (Kanto chemicals) and $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (Furuya metal) were used as starting materials. For the preparation of hydrous titania by hydrolysis the following solutions were used: TiCl_4 diluted with the same volume of 1 mol l^{-1} of HCl and consequently with distilled water so that the concentration of Ti^{4+} was about 0.7 mol l^{-1} calculated as TiO_2 . To this solution a 2 mol l^{-1} ammonia was added drop by drop. For the ruthenium component, a 1 mol l^{-1} ruthenium chloride solution was prepared by dissolving $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ in 0.1 N hydrochloric acid. The ruthenium content was determined gravimetrically using RuO_2 as the species determined gravimetrically.

The mixed solution in the molar ratio $\text{Ti}:\text{Ru} = 9:1$ was prepared by mixing the dissolved Ti and Ru chlorides in the respective overall ratio. To this solution the 2 mol l^{-1} ammonia was added dropwise in an abundant amount. The precipitate obtained was subsequently washed, filtered and dried at 120°C .

2.2. Methods used for sample characterisation

Taking into account that ETA is a less common method, we shall describe its principles to the extent that is necessary for the discussion and interpretation of the results.

ETA [7,8] involves the measurement of radon release rate from samples previously labelled. The samples were labelled 3 weeks prior to ETA measurements using the adsorption of traces of ^{228}Th and ^{224}Ra on the sample surface from acetone solution. The specific activity of a sample was 10^5 Bq per ml . Atoms of radon, ^{220}Rn , are formed by the spontaneous alpha-decay of ^{228}Th and ^{224}Ra . The ^{224}Ra and ^{220}Rn atoms are incorporated into the sample to a maximum

depth of 120 nm due to the recoil energy (85 keV per atom) which the atoms gain by the alpha spontaneous decay.

A part of the radon atoms formed by spontaneous alpha-decay of radium is directly released from the sample by recoil. Another part of the radon atoms is trapped in the lattice defects, such as vacancy clusters, grain boundaries and pores, and can be released from the sample by diffusion. The defects in the solids serve both as traps and diffusion paths for radon. The radon release rate depends on the surface area and on the radon diffusion parameters in the solid [8].

The rate of radon release from the sample (called the emanation release rate, E) is expressed in a simplified way as follows:

$$E = E_{\text{recoil}} + E_{\text{diffusion}} = S[K_1 + K_2 \cdot \exp(-Q/2RT)], \quad (1)$$

where E_{recoil} is the part of the radon release due to recoil, $E_{\text{diffusion}}$ the diffusion part of the released radon, S the surface area, K_1 a constant proportional to the penetration depth of Rn recoiled atoms, K_2 a constant comprising the decay constant of radon, the pre-exponential factor of the radon diffusion coefficient, Q the activation energy of radon diffusion in the sample, R the molar gas constant, and T the temperature in absolute Kelvin scale.

Consequently, processes that can be investigated by means of ETA are those accompanied by changes of surface area and/or microstructure of the solid samples, affecting the inert gas diffusion release from the solids. For titania powder a linear relationship of E values measured at room temperature and the surface area values determined by BET method from the nitrogen adsorption was experimentally found [9]. For low temperatures, where no thermal diffusion of radon in the matrix is assumed to take place, the values of E are proportional to the surface area. For temperatures where radon diffusion in the matrix takes place, such a direct relationship cannot be assumed.

An increase of the radon release rate, E , corresponds to an opening of the structure and/or an increase in the surface area, whereas a decrease in E corresponds to a densification of the structure, closing pores and/or decrease in the surface area of the sample.

The ETA-DTA measurements were carried out at the Nuclear Research Institute Řež using a modified

NETZSCH DTA 404 equipment. The heating rate of 5 K min^{-1} , the cooling rate 2.5 K min^{-1} , and the argon flow rate of 40 ml min^{-1} were used. During the ETA measurements, the labelled sample of 0.1 g was situated in a corundum crucible immersed in a constant flow of argon, which carried the radon released from the sample into the measuring chamber of radon radioactivity [7].

The TG measurements were carried out at NIRIM Tsukuba in the same experimental conditions as the ETA-DTA measurements, using Rigaku TAS 300 apparatus. The XRD patterns were obtained by JEOL equipment using $\text{CuK}\alpha$ Ni filtered radiation. For microstructure characterisation the TEM Philips 201 equipment was used at the Institute of Inorganic Chemistry, Řež. The surface area was determined by means BET method from the nitrogen adsorption measurement using Coulter SA 3100 apparatus.

2.3. Characterisation of feed samples

From the XRD patterns it can be seen that the hydrous TiO_2 , resulting after hydrolysis and drying at 120°C , consisted of poorly crystallised anatase. In the co-precipitated oxides of the molar composition, $\text{Ti:Ru} = 0.9:0.1$, a mixture of poorly crystalline anatase and an amorphous solid solution of ruthenia and titania was present.

According to the photomicrographs of the feed samples obtained by TEM, the $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ (where $n = 0.66$) sample consisted of 1–5 μm large agglomerates composed of nanosize grains ($\sim 5 \text{ nm}$). Surface area of this sample was determined as $S = 173 \text{ m}^2 \text{ g}^{-1}$. The microstructure of the mixed hydrous oxide $(\text{TiO}_2)_{0.9}(\text{RuO}_2)_{0.1} \cdot n\text{H}_2\text{O}$ (where $n = 1.30$) sample was similar to that of hydrous titania: the agglomerates were composed of slightly smaller primary grains than 5 nm. Surface area of the mixed oxide samples was $S = 213 \text{ m}^2 \text{ g}^{-1}$.

3. Results and discussion

3.1. Thermal behaviour of hydrous titania

From the TG results presented as the full line in Fig. 1, it follows that the hydrous titania ($\text{TiO}_2 \cdot n\text{H}_2\text{O}$) loses water continuously from 60°C to 400°C (the total

mass loss is 12.9%). As it follows from the TEM photomicrographs, (Fig. 2), the primary grains of the titania samples heated to 300°C did not change in size, as compared with the feed sample, nevertheless the TEM photomicrographs indicated that water adsorbed on the surface and intergranular space was released. The surface area of the sample heated to 300°C was $S = 148.4 \text{ m}^2 \text{ g}^{-1}$. At the temperature of 400°C a partially crystalline anatase phase was detected by XRD. In the sample heated to 500°C the size of primary grains increased (Fig. 2c). The surface area of this sample decreased ($S = 89.7 \text{ m}^2 \text{ g}^{-1}$), as compared with the sample heated to 300°C . A partially crystalline anatase phase was present in the sample heated to 500°C . In the titania sample heated to 800°C , well developed crystals of anatase of the size $\sim 0.1 \mu\text{m}$ were observed. The surface area of the sample heated to 800°C was $S = 41.6 \text{ m}^2 \text{ g}^{-1}$. In the sample heated to 1000°C the crystal size increased to $1 \mu\text{m}$. The presence of rutile was detected by XRD in the sample heated to 1000°C .

The microstructure changes of the titania sample during heating were characterised by means of ETA as follows (see the full line in Fig. 3). The increase of Rn release rate, E , in the temperature interval $20\text{--}300^\circ\text{C}$ reflected the process of the surface liberation from water under in-situ conditions of heating. In the temperature interval $300\text{--}420^\circ\text{C}$ no significant changes of E were observed. On further heating to 800°C a decrease in E was monitored, corresponding to the growth of the primary grains of anatase and its subsequent crystallisation.

The ETA results are in agreement with the surface area and TEM characteristics of the microstructure of titania heated to selected temperatures in the range $400\text{--}800^\circ\text{C}$. The annealing of surface roughness and crystallisation of anatase was monitored by means of ETA under in-situ conditions of sample heating.

At 850°C , the onset of the enhanced Rn release by thermal diffusion was observed on the ETA curve (Fig. 3). The decrease of E values starting at 910°C indicated the intense growth of the primary grains, accompanying the phase transformation of anatase to rutile. At further heating above 980°C the E increase due to the diffusion of Rn in the rutile structure was measured. This ETA characterisation of titania thermal behaviour agrees well with the results obtained earlier by one of the authors [10].

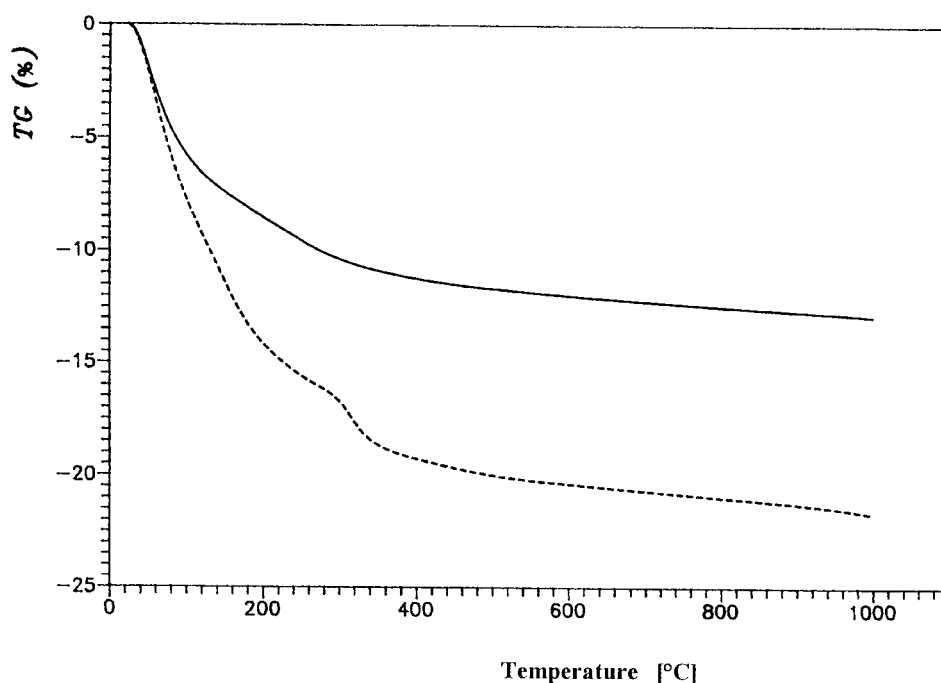


Fig. 1. Results of thermogravimetry obtained during heating in argon of hydrous titania (full line) and hydrous titania containing 10% of ruthenia (dotted line). Heating rate 5 K min^{-1} .

3.2. Thermal behaviour of hydrous titania containing 10% of ruthenia

The thermal behaviour of hydrous titania containing ruthenia in the molar ratio $\text{Ti:Ru} = 9:1$ differs from that of hydrous titania, described in the previous paragraph. As indicated by the TG results (see dotted line in Fig. 1), the mass loss taking place in the temperature range $60\text{--}400^\circ\text{C}$ represents 20% of the initial sample mass. From the TEM photomicrographs of the sample heated to 400°C (Fig. 4) it follows that the primary grain size did not practically differ from that of the initial hydrous sample. Loss of water from the surface and intergranular space was observed. On further heating of the sample, significant growth of the grains takes place resulting in the fully crystalline solid solution of ruthenia–titania with the rutile structure.

This statement is supported by XRD patterns as well as by an exothermic DTA effect observed in the temperature range $430\text{--}480^\circ\text{C}$, corresponding to crystallisation.

From the ETA results presented in Fig. 3 differences in the kinetics of the microstructure changes between hydrous titania containing 10% ruthenia and hydrous titania were monitored under in-situ conditions of heating. The microstructural changes of hydrous titania containing 10% ruthenia were characterised as follows. In the temperature interval $60\text{--}230^\circ\text{C}$ a more intense initial increase of radon release rate E was observed (see dotted line, Fig. 3) as compared to hydrous titania. This increase of E corresponds to the liberation of the surface initially covered by water molecules, and to a free surface area increase due to the dehydration of the sample (the mass loss being more intense with the titania containing 10% ruthenia than hydrous titania only — see TG results in Fig. 1).

Consequently, the decrease of E measured during the sample heated above 300°C corresponds to the surface area decrease. The surface area of the sample heated to 380°C was $S = 250 \text{ m}^2 \text{ g}^{-1}$. At 400°C the onset of the crystallisation was determined as the temperature of a change in the slope of the ETA curve.

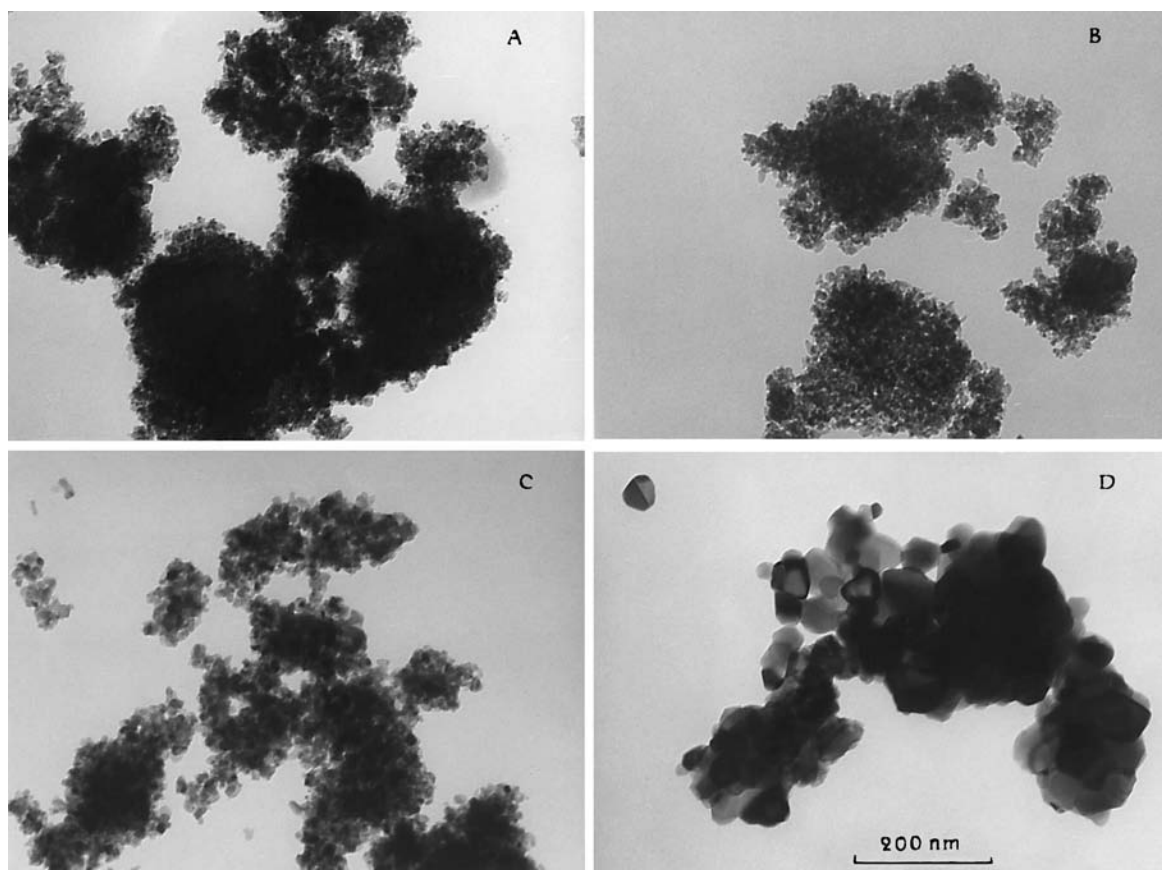


Fig. 2. TEM photomicrographs (magnification 100 000 \times) of titania samples heated to (a) 120°C — feed titania sample, (b) 300°C, (c) 500°C and (d) 800°C.

By DTA, the crystallisation interval was determined as 430–480°C, corresponding to the crystallisation in the bulk. The intense decrease of Rn release rate continued up to 530°C, followed by a slower decrease in E up to 800°C. The surface area of the intermediate product heated to 580°C was 50.9 m² g⁻¹. The ETA results characterising the intermediate products heated to 380°C and 580°C, respectively, were in agreement with surface area and TEM microstructure characterisation of the samples (see Fig. 4b and c, respectively).

The increase of radon release rate, E , observed on further heating above 830°C indicated the temperature of the onset of the diffusion release of Rn from the sample. In the temperature range 830–1000°C, a more intense increase in E takes place with the (TiO₂)_{0.9}–

(RuO₂)_{0.1} sample as compared to the titania sample (Fig. 3). The differences in the diffusion mobility of Rn atoms reflected the different dynamic properties of the respective samples in this temperature range.

In addition, ETA was used to provide a more detailed investigation of microstructure changes during heating of hydrous titania containing 10% ruthe-
nia. In order to obtain information about the microstructural changes, the intermediate products heated to selected temperatures (namely 380°C, 580°C, and 980°C) were subjected to ETA measurements during heating to these temperatures and subsequent cooling (Fig. 5a–c).

The temperature dependence of the radon release rate, E , in Fig. 5a monitored the thermal behaviour of the sample during heating from 30°C to 380°C: the

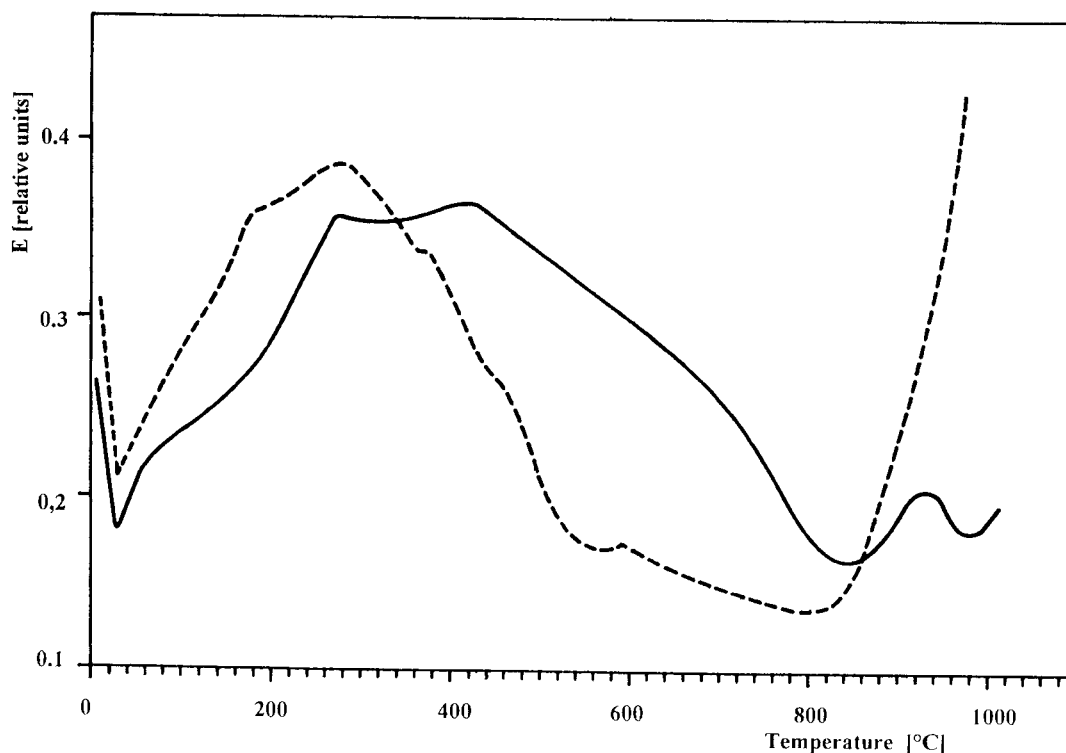


Fig. 3. Results of ETA measured during heating in argon of hydrous titania (full line) and hydrous titania containing 10% of ruthenia (dotted line). Heating rate 5 K min^{-1} .

increase of E observed in the temperature range $30\text{--}170^\circ\text{C}$ corresponds to the increase of the free surface area resulting after water release from the sample. The slowing down of E indicated that parallel to the water release from the bulk sample, surface annealing takes place (surface layers to the maximum depth of 100 nm were labelled with radon atoms). The loss of 19% of the initial sample mass took place during this heating to 380°C .

From the ETA curve measured on a sample cooled from 380°C to room temperature it follows that the microstructural changes are irreversible. The differences between the E values measured at room temperatures before and after sample heating to 380°C are in a good agreement with the surface area measurements and TEM results (Fig. 3)

Fig. 5b represents the ETA results measured when the sample previously heated to 380°C was reheated to 580°C . The increase in E was observed with a much lower slope than in the first heating run, corresponding to radon diffusion in opened pores and possibly to an

increase in the surface area after the release of the remaining water molecules. The loss of 4.4% of the sample mass took place during heating to 580°C . The more intense decrease in E observed during sample heating above 430°C was ascribed to the crystallisation of the sample.

The irreversible character of these changes was confirmed by the ETA results measured during sample cooling.

The ETA results measured during heating to 980°C of the sample previously heated to 580°C are presented in Fig. 5c. The increase in E values corresponds to the radon release from the surface and opened pores. The decrease in E observed on heating above 700°C monitored annealing surface roughness and structure irregularities.

The increase in E observed during heating above 850°C is due to heat stimulated radon diffusion. The effect at 950°C was ascribed to the partial dissociation of the sample due to the loss of oxygen (during heating in the temperature range from 20°C to 950°C , a mass

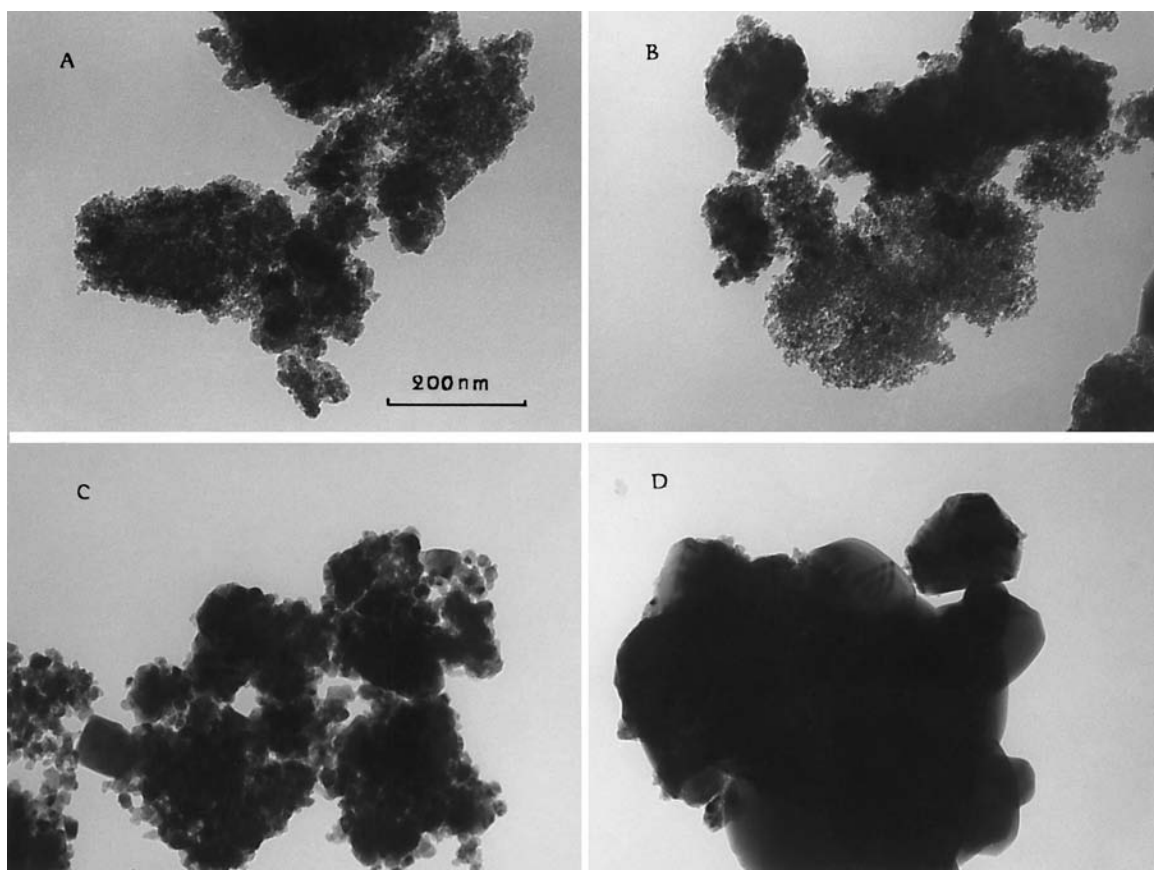


Fig. 4. TEM photomicrographs (magnification 100 000 \times) of $(\text{TiO}_2)_{0.9}\text{-(RuO}_2)_{0.1}$ samples heated in argon to (a) 120 $^\circ\text{C}$ — feed sample, (b) 380 $^\circ\text{C}$, (c) 580 $^\circ\text{C}$, and (d) 980 $^\circ\text{C}$.

loss of 0.7% of the sample mass took place). The ETA cooling curves reflected radon diffusion from the sample heated to 980 $^\circ\text{C}$.

From the comparison of the results in Fig. 5a–c and the dotted line in Fig. 4, good reproducibility of the ETA results can be seen.

It was of interest to compare the transport properties of the $(\text{TiO}_2)_{0.9}\text{-(RuO}_2)_{0.1}$ sample and its intermediate products prepared after heating to the respective temperatures. The values of the activation energy of radon diffusion in the samples were determined from the Arrhenius plot representing $\log(E - E_{25})$ vs. $(1/T)$. The curves plotted using the ETA results measured during cooling the samples previously heated to 380 $^\circ\text{C}$, 580 $^\circ\text{C}$ and 980 $^\circ\text{C}$, respectively, are presented in Fig. 6.

The values of the activation energy, Q , of radon diffusion calculated from the slope of the Arrhenius plots (Fig. 6) are summarised in Table 1.

The low values of Q correspond to the high mobility of radon (atom size 0.4 nm) in the low temperature range, 100–380 $^\circ\text{C}$, in the porous and disordered sample. The loosened structure of the sample heated to 380 $^\circ\text{C}$ was characterised by high radon mobility. A slightly densified structure of the sample resulted after heating to 580 $^\circ\text{C}$. A compacted (sintered) sample resulted after the heating to 980 $^\circ\text{C}$.

The increase in Q values corresponds to the annealing of structure irregularities and ordering of the disordered structure. The values of the activation energy of radon diffusion of the heat treated samples presented in Table 1 are in good agreement

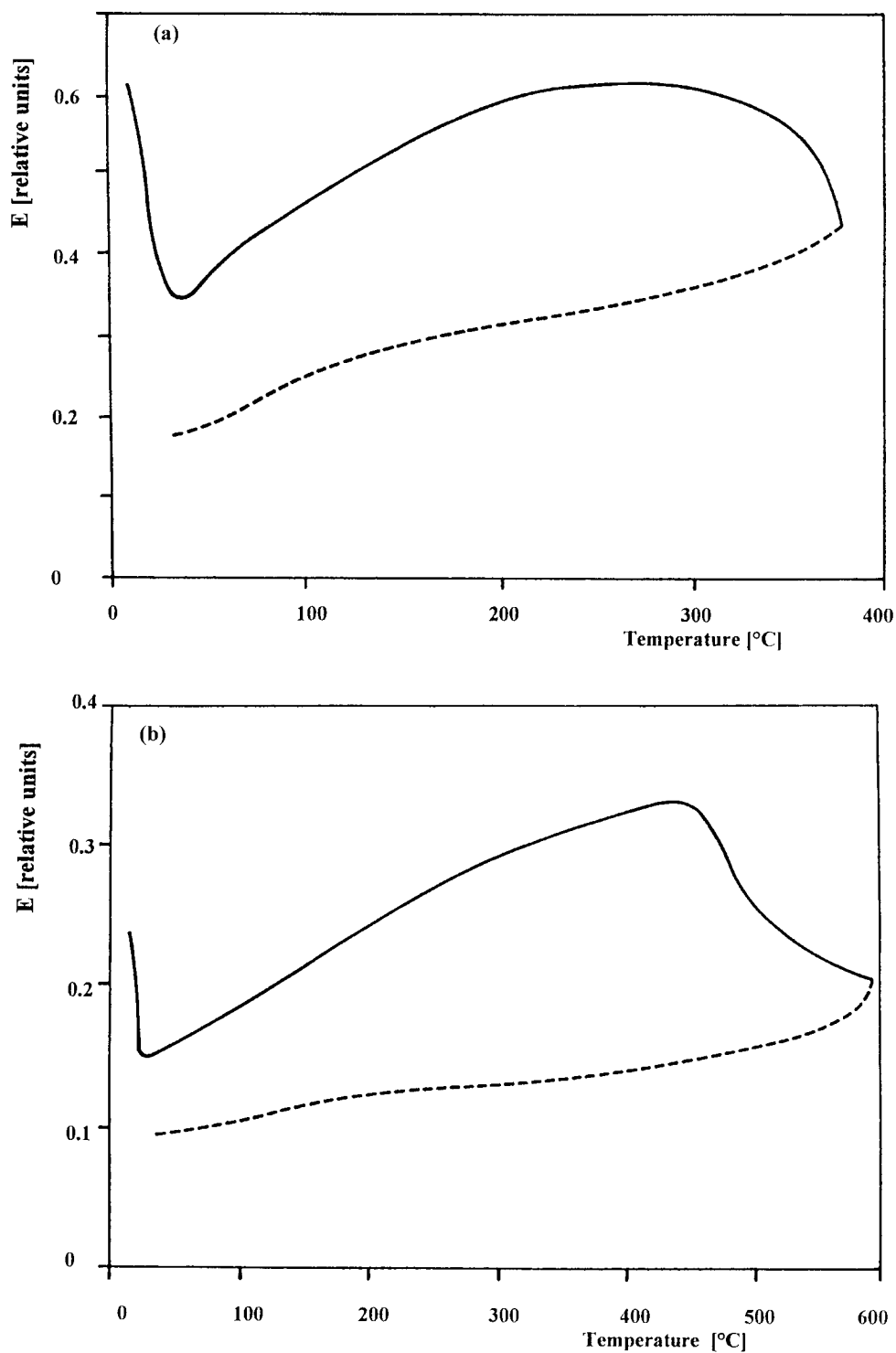


Fig. 5. Results of ETA measured during heating and subsequent cooling of hydrous titania containing 10% ruthenia to selected temperatures: (a) 380°C, (b) 580°C, and (c) 980°C. Full lines represent heating curves, dotted lines represent cooling curves.

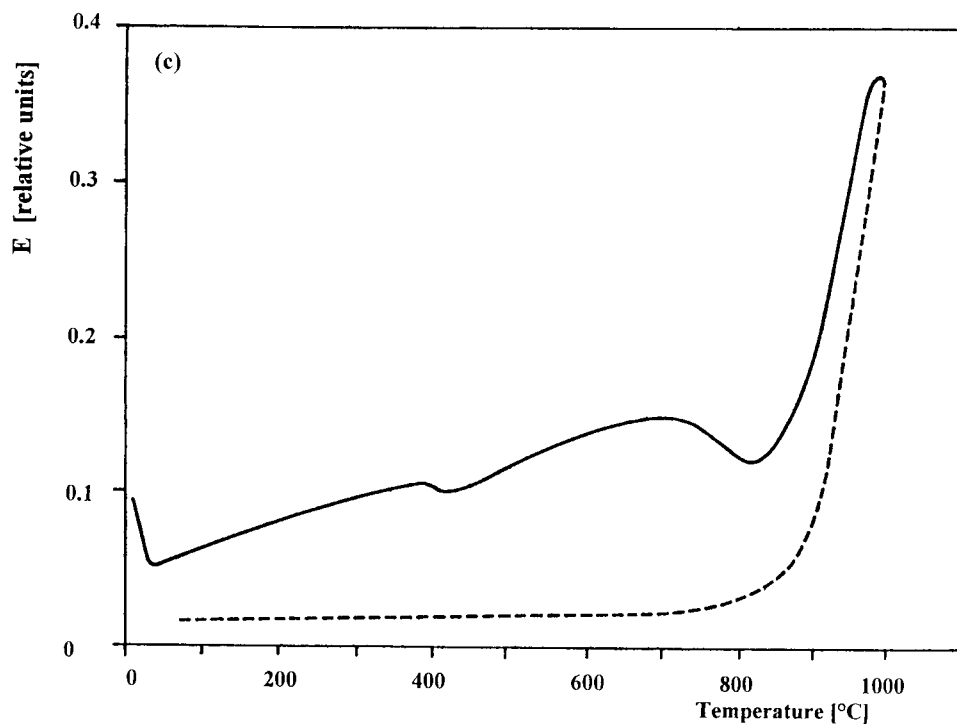


Fig. 5. (Continued).

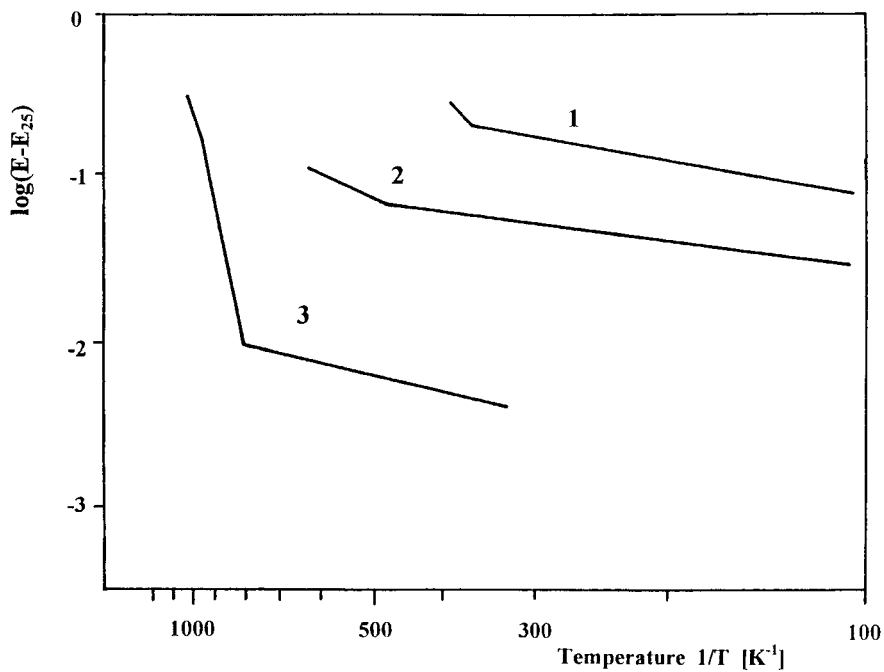


Fig. 6. Temperature dependence of radon release rate $\log(E - E_{25})$ vs. $(1/T)$ due to the radon diffusion from $(\text{TiO}_2)_{0.9}-(\text{RuO}_2)_{0.1}$ samples heated to the temperatures of: 380°C (curve 1), 580°C (curve 2), and 980°C (curve 3). From the slopes of the linear parts of the plots the values of activation energy Q of radon diffusion were calculated (Table 1).

Table 1

Values of the activation energy, Q , of radon diffusion measured in $(\text{TiO}_2)_{0.9}\text{--}(\text{RuO}_2)_{0.1}$ sample heated to temperatures 380°C, 580°C and 980°C

Temperature of sample heating (°C)	Values of Q (kJ mol^{-1}) determined for the temperature range
380	15 ± 4 (for the interval 100–380°C)
580	11 ± 4 (for the interval 100–500°C); 46 ± 2 (for the interval 500–580°C)
980	14 ± 4 (for the interval 200–600°C); 398 ± 1 (for the interval 800–980°C)

with the TEM characteristics of the microstructure (Fig. 4).

4. Conclusions

The ETA results monitored microstructural changes taking place during heating of hydrous titania and titania containing 10% ruthenia. The in-situ characterisation of the microstructure changes obtained from the ETA results is in an agreement with the results of thermogravimetry and DTA, describing their dehydration and crystallisation, respectively.

The TEM and XRD characteristics of the samples heated to selected temperatures support the ETA results. The activation energy of radon diffusion was determined making it possible to characterise annealing structural irregularities of the samples investigated. The ETA results have been used in the design of new effective photocatalysts, especially in the determination of optimum conditions for their thermal treatment.

Acknowledgements

This work was carried out in the frame of the cross-over research project on underlying technology of

nuclear energy promoted by the Science and Technology Agency of Japan and the bilateral co-operation in Science and Technology between the Czech Republic and Japan supported by the Ministry of Education of the Czech Republic.

References

- [1] A. Fujishima, K. Honda, *Nature (London)* 238 (1972) 37.
- [2] A. Fujishima, K. Honda, *Bull. Chem. Soc. Jpn.* 44 (1971) 148.
- [3] K.M. Glassford, J.R. Chelikovski, *Phys. Rev. B* 47 (1993) 12 550.
- [4] T. Kawai, T. Sakata, *J. Chem. Soc., Chem. Commun.* (1980) 694.
- [5] T. Kawai, T. Sakata, *Chem. Phys. Lett.* 80 (1981) 341.
- [6] T. Kawai, T. Sakata, *Chem. Phys. Lett.* 72 (1980) 87.
- [7] V. Balek, *Thermochim. Acta* 192 (1991) 1.
- [8] V. Balek, J. Tölgyessy, in: *Wilson and Wilson's Comprehensive Analytical Chemistry, Part XII C*, Elsevier, Amsterdam, 1984, 304 pp.
- [9] V. Balek, in: I. Buzás (Ed.), *Thermal Analysis, Proc. of Fourth Int. Conf. on Thermal Analysis, Budapest, 1974*, vol. 2, Akadémiai Kiadó, p. 351.
- [10] V. Balek, *Sprechsaal — Int. Ceramics and Glass Magazine* 116 (1983) 978.