Journal of Thermal Analysis and Calorimetry, Vol. 80 (2005) 671–677

THERMAL BEHAVIOUR OF THE PRECURSORS OF RUTHENIA–TITANIA BASED MIXED OXIDES

N. K. Labhsetwar[1*]*, V. Balek*[2]*, S. Rayalu*[1]*, T. Terasaka*[3]*, A. Yamazaki*[4]*, J. Šubrt*[2]*, H. Haneda*[3] *and T. Mitsuhashi*[3]

[1]National Environmental Engineering Research Institute, Nehru Marg, Nagpur 440020, India
[2]Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic 250 68 Řež, Czech Republic
[3]Advanced Materials Laboratory, National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
[4]Department of Resources and Environment Engineering, School of Science and Engineering, Waseda University, Tokyo 169-8555, Japan

Studies on ruthenia–titania based materials have been attractive because of their catalytic properties as well as due to the possibility of solid solution formation. Samples of pure ruthenia and ruthenia containing various amounts of titania (10–70 mol%) were investigated during heating of their hydroxide precursors from 20 to 800°C in air using emanation thermal analysis (ETA), thermogravimetry (TG), and differential thermal analysis (DTA). The resulting mixed oxide type materials were characterized by X-ray diffraction (XRD), which indicate the presence of three ruthenia–titania phases. The onset temperature of the crystallization of materials was identified by ETA results, whereas DTA effects characterized the crystallization in bulk of the samples. A good agreement was found between the ETA results and other characterization techniques used. ETA results, indicating the microstructural changes in surface and subsurface of ruthenia–titania based catalytic materials, can be used for optimization of their synthesis protocols to achieve the better physical properties.

Keywords: *DTA, emanation thermal analysis, ruthenia, ruthenia–titania, solid solution, thermogravimetry*

Introduction

Ruthenium in both metallic and oxide forms have been extensively studied for various catalytic as well as other reactions of commercial and environmental importance [1–6]. Ruthenium dioxide (RuO_2) or ruthenia also shows good catalytic activity for many oxidation reactions. However, ruthenia tends to form volatile oxides at higher temperature under oxidative atmosphere, which restricted its high temperature applications. Therefore, the samples of ruthenia containing various amount of titania were investigated in a view to improve the physical and catalytic properties. We have already reported the preparation of rutile type solid solution in ruthenia–titania based materials by heating of their hydrous precursors under nitrogen atmosphere [7]. We have also studied the microstructure and surface development during the formation of RuO_2–TiO_2 type materials prepared by heating of their precursors in argon [8]. To obtain the optimal properties of these materials for catalytic applications, it is important to study in detail the surface and subsurface processes during their formation. This also helps to optimize their synthesis protocols and to obtain the desired properties e.g. high surface area.

This paper reports the preparation of ruthenia–titania based materials by heating of their hydroxide precursors in air. Various techniques, such as thermogravimetry (TG), differential thermal analysis (DTA) and emanation thermal analysis (ETA), were used in order to elucidate the processes during the preparation of pure RuO_2 and RuO_2 containing various amount of TiO_2. As reported in our previous publications [9–11], the ETA is a useful method for the in situ characterization of surface development and sub-surface microstructure changes in the materials during their synthesis. In the present study, the ETA has been successfully used as a complementary technique to other methods for characterizing the early stages of crystallization of pure ruthenia and ruthenia–titania based materials. The ETA technique has been used to obtain information about microstructure development during heating of layered double hydroxides [12], aluminium hydroxide [13], titania based hydrous oxide [14]. This technique has also been reported for the characterization of precursors for preparation of catalysts, sorbents and other advanced inorganic materials [15,16]. An excellent correlation between ETA data and surface area values measured by nitrogen adsorption and evaluated by B.E.T. method was demonstrated [12].

Experimental

Samples preparation

Reagent grade $RuCl_3 \cdot nH_2O$ (Furuya Metal, Japan) and $TiCl_4$ (Kanto Chemicals, Japan) were used as starting

---

* Author for correspondence: nitin_neeri@yahoo.com

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

materials. Ruthenium chloride solution was prepared by dissolving $RuCl_3 \cdot nH_2O$ in 0.1N hydrochloric acid. For the preparation of hydrous ruthenia–titania samples, the solutions of the dissolved Ti and Ru chlorides in the respective overall ratios were used. The mixed solution was added dropwise to 2N aqueous ammonia solution. The precipitates thus obtained for various compositions were washed, filtered and dried at 120°C. The resulting hydrous precursors of pure ruthenia ($RuO_2 \cdot nH_2O$) and ruthenia containing 10, 30, 50 and 70 mol% of titania were used for the TG, DTA and ETA analysis. The anhydrous oxide samples of pure ruthenia and ruthenia containing various amount of titania were prepared by heating the respective hydrous precursors in air from room temperature to two different temperatures viz. 500 and 800°C and by subsequent isothermal heating at the respective temperatures for one hour.

Samples of the hydrous oxide precipitates used for the ETA measurements were first labelled by adsorption of the radionuclides of ^{228}Th and ^{224}Ra from acetone solutions of their nitrates. The acetone was evaporated at approximately 40°C, immediately after the labelling. The specific activity of the labelled samples was 10^5 Bq g^{-1}.

Characterization method and equipments

ETA is based on the measurements of the release of radon (^{220}Rn) from the samples previously labelled [9–11]. The ^{220}Rn atoms were formed by the spontaneous α-decay of ^{224}Ra. It was determined by means of Monte Carlo method using TRIM code [12] that the maximum depth of the labelling by ^{224}Ra and ^{220}Rn recoiled atoms was 60 nm. The radon release rate, E (also called as emanating rate), can be expressed in a simplified way [9, 10] as follows:

$$E=E_{\text{recoil}}+E_{\text{diffusion}}=S[K_1+(D/\lambda)^{1/2}K_2] \qquad (1)$$

where E_{recoil} is the part of the radon release due to recoil, $E_{\text{diffusion}}$ is the diffusion part of the released radon, S is surface area, K_1 is a temperature independent constant, proportional to the penetration depth of ^{220}Rn recoiled atoms, D is the coefficient of radon diffusion in the sample, λ is the ^{220}Rn decay constant (λ=0.12 s^{-1}), K_2 is a temperature dependent constant. Further details about this technique are given in our previous publications [9–11].

The Netzsch ETA-DTA Equipment type 404 was used for ETA measurements. The sample amount of 0.1 g was heated in air at the rate of 5 K min^{-1} in a corundum crucible being overflowed by the constant flow of air (50 cm^3 min^{-1}), which carried the radon released from the sample into the measuring chamber of radon radioactivity. The TG and DTA measurements were carried out in air at the heating rate of 5 K min^{-1} using Rigaku equipment model TG-8110. Powder X-ray diffraction data were recorded at room temperature on a Rigaku Rint-2200V/PC using Bragg–Brentano geometry with CuK_α radiation (40 kV, 50 mA) in a 2θ range 10–60° at a rate of 2.0 K min^{-1}. SEM microphotographs were obtained by using the JEOL S-5000 FE-SEM Equipment, Japan, at an acceleration voltage of 10 kV.

Results and discussion

Formation and crystallization of anhydrous pure ruthenia and ruthenia containing 10–70 mol% of titania was investigated by using TG, DTA, ETA and XRD techniques. Figure 1 (curves 1–5) presents the XRD patterns for pure ruthenia and ruthenia containing various amounts of titania samples prepared by heating in air from room temperature to 500°C and subsequent isothermal heating for 1 h. As it follows from the XRD patterns (Fig. 1, curves 1 and 2), a well crystallized ruthenia phase having rutile structure was found in both pure RuO_2 and $(RuO_2)_{0.9}$–$(TiO_2)_{0.1}$ samples. It correspond to RuO_2 as well as $(RuO_2)_{0.9}$–$(TiO_2)_{0.1}$ solid solution in the later sample which is in agreement with the findings by

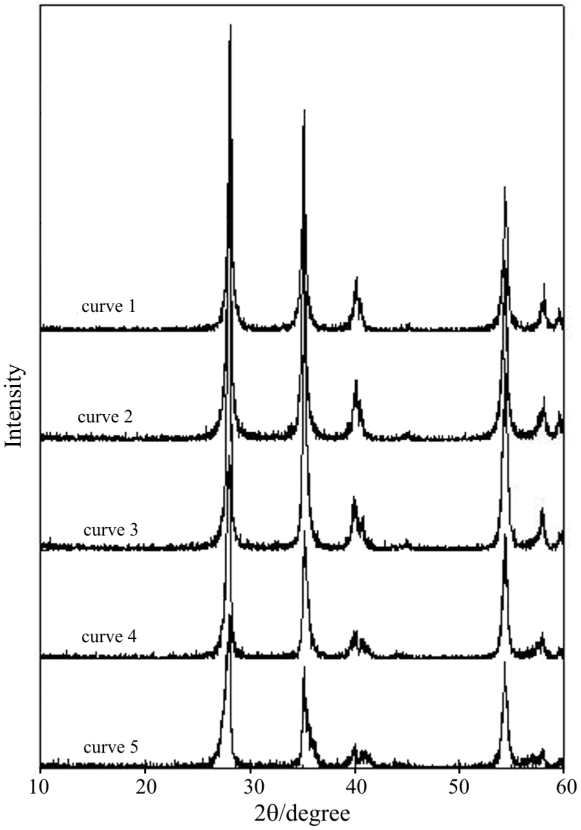

Fig. 1 X-ray powder diffraction patterns for samples heated at 500°C, curve 1 – pure ruthenia, curve 2 – ruthenia containing 10 mol% titania, curve 3 – ruthenia containing 30 mol% titania, curve 4 – ruthenia containing 50 mol% titania, curve 5 – ruthenia containing 70 mol% titania

other authors [18, 19] that ruthenia with 10 mol% (and even 20 mol%) of titania form solid solutions with rutile structure. From Fig. 1 (curves 3–5) it followed that the well defined titania peaks could not be observed in the XRD patterns for the ruthenia containing 30, 50 and 70 mol% of titania probably due to the overlapping of XRD peaks. Nevertheless a relative lowering of intensity of major RuO_2 peaks was observed in these samples while appearance of titania peaks was observed in samples containing higher amount of titania.

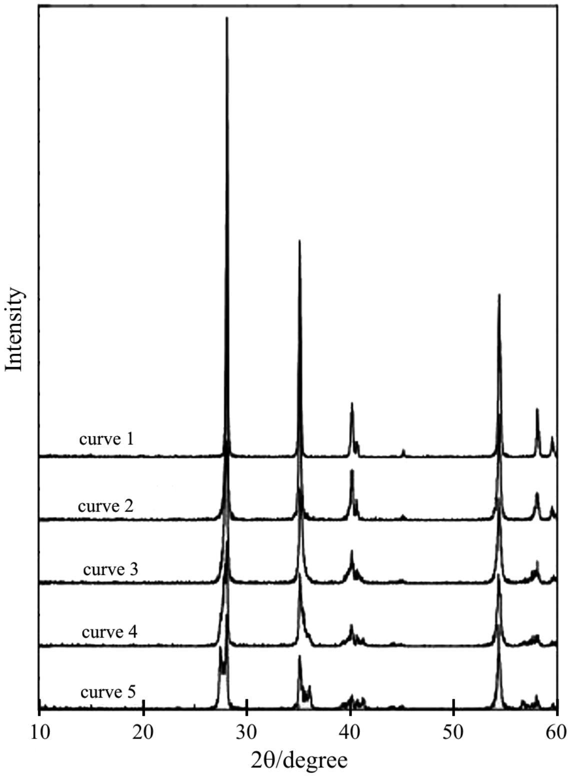

Fig. 2 X-ray powder diffraction patterns for samples heated at 800°C, curve 1 – pure ruthenia, curve 2 – ruthenia containing 10 mol% titania, curve 3 – ruthenia containing 30 mol% titania, curve 4 – ruthenia containing 50 mol% titania, curve 5 – ruthenia containing 70 mol% titania

The XRD patterns of the samples prepared by heating of the precursors in air from room temperature to 800°C for 1 h (Fig. 2, curves 1–5) show relatively sharper peaks indicating the formation of highly crystalline materials at 800°C. The decrease in intensity of RuO_2 peaks was observed in samples containing increasing amount of titania. We have attempted to resolve the XRD patterns of sample containing 50 mol% of titania to further identify the phases, especially the solid solutions. These results are presented in Fig. 3 along with the phases identified. These results confirmed the presence of three phases, namely ruthenia rich solid solution, titania rich solid solution and an intermediate crystalline phase, respectively. These phases may be co-existing in both the samples heated at 500 and 800°C respectively, however, their presence was clear in the later sample with better peak separation. We know that rutile type TiO_2 can form wide range of solid solutions with Ru^{4+} [7] while it is relatively difficult to observe solid solution formation in anatase phase. Although Gibbs phase rule describes the possibility of only two solid phases to coexist in binary systems, however, the present samples are metastable and co-existence of three phases appears to be existing. It was not possible to index the peaks separately for various solid solution phases in other samples, due to their overlapping. It is inferred from the XRD results that the hydrous precursors of ruthenia and ruthenia–titania based samples studied were initially amorphous. No XRD lines were observed with the samples heated up to about 300°C. The well crystalline samples were obtained only after heating in air at about 500°C [15]. This is in agree-

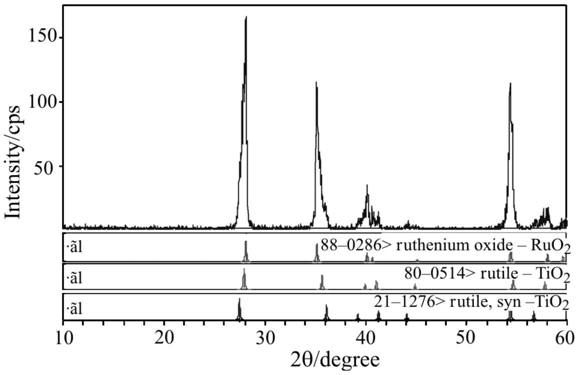

Fig. 3 Phase analysis for XRD results of ruthenia containing 50 mol% titania

Identified phases

Phase	Formula	JCPDS file	System	S. G.	*a*/Å	*c*
ruthenium oxide	RuO_2	PDF #88-0286	tetragonal	136	4.497	3.105
rutile	TiO_2	PDF #82-0514	tetragonal	136	4.508	3.027
rutile, syn	TiO_2	PDF #21-1276	tetragonal	136	4.593	2.959

ment with the previous studies [16]. Further detailed investigations are required to properly characterize the solid solution formation at different temperatures for the ruthenia–titania based systems.

TG/DTA curves of the hydrous precursors measured during their heating in air from room temperature to 800°C are presented in Figs 4–8. The mass loss observed in the range 50–500°C for all the samples was due to dehydration that took place in three steps. The temperature ranges of the dehydration steps observed for pure ruthenia and ruthenia containing 10 mol% of titania were almost identical viz.: 50–260, 260–380 and 380–500°C. The last dehydration step was accompanied by crystallisation, as indicated by DTA exothermic effects (Figs 4 and 5). For $RuO_2 \cdot nH_2O$, the exothermal effect was observed at 390–420°C as the peak initial-peak top temperatures while it was observed at 380–430°C for the $(RuO_2)_{0.9}$–$(TiO_2)_{0.1} \cdot nH_2O$ sample. This is in agreement with the findings in our previous studies [21].

For hydrated precursors containing 30 mol% titania, two exothermic peaks were observed on DTA (Fig. 6) viz. at 325–380 and 430–450°C respectively, indicating two-step crystallization. The first step may be ascribed to the crystallization of solid solution and another to the pure ruthenia phase crystallization, although there could be total three phases formed i.e. pure ruthenia, pure titania and solid solution, considering the solid solubility limit of approximately 20 mol%. In this way the DTA results indicated the formation of two phases out of three possible phases, two of which could be formed at similar temperature range. Similarly, two exothermic effects were observed on heating of both the hydrous ruthenia containing 50 mol% of titania and the hydrous ruthenia containing 70 mol% of titania, however, in slightly different temperature ranges (Figs 7 and 8). As it follows from DTA results in Figs 7 and 8, the first exothermic effects were observed for the mentioned samples at the temperature ranges 335–370°C and 325–380°C, whereas the second exothermic effects were observed at the temperature ranges 460–500 and

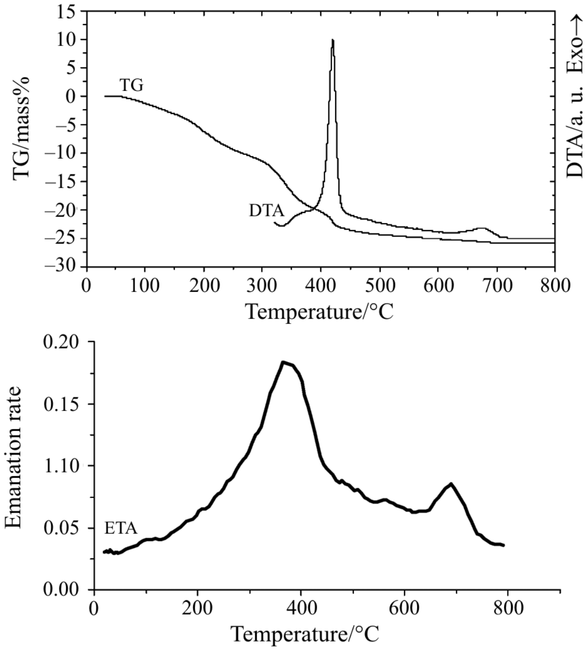

Fig. 4 TG-DTA and ETA results of hydrous precursors for pure ruthenia in air

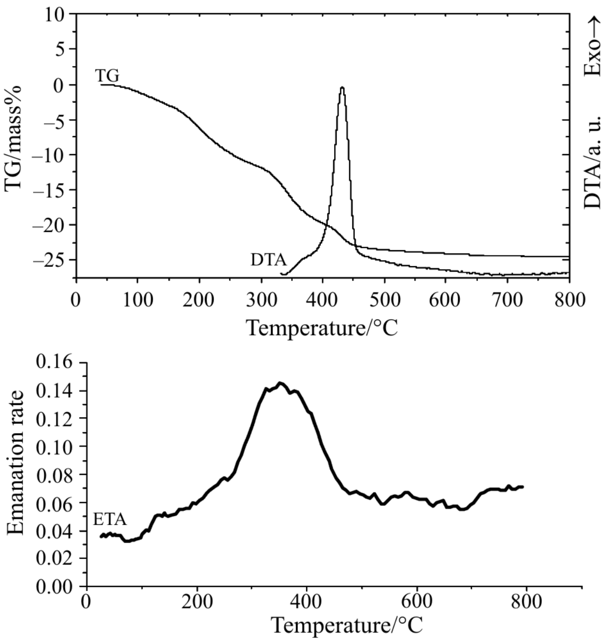

Fig. 5 TG, DTA and ETA results of hydrous precursors for ruthenia containing 10 mol% of titania

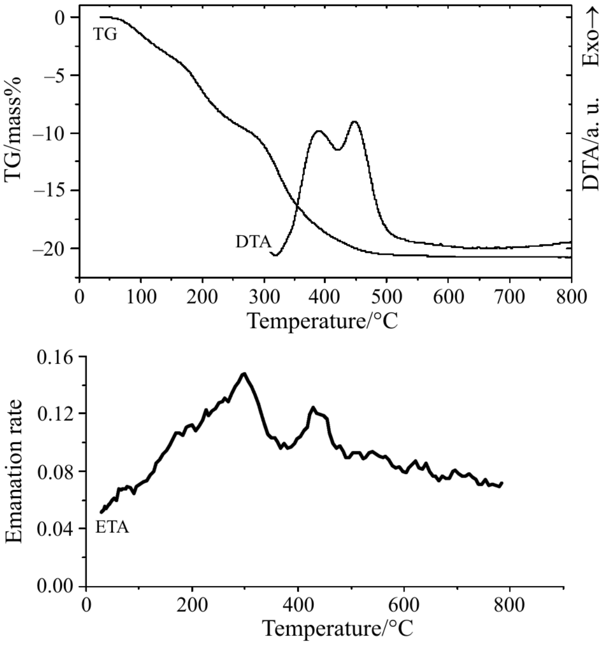

Fig. 6 TG, DTA and ETA results of hydrous precursors for ruthenia containing 30 mol% of titania

Table 1 DTA results for hydrated precursors of ruthenia-titania based materials

	Temperature range/°C	
	1st crystallization process	2nd crystallization process
Sample	DTA exothermic effect	DTA exothermic effect
pure ruthenia	390–420	630–675
ruthenia containing 10 mol% titania	380–430	
ruthenia containing 30 mol% titania	325–380	430–450
ruthenia containing 50 mol% titania	335–370	460–500
ruthenia containing 70 mol% titania	325–380	460–505

460–505°C respectively. The temperature ranges for the crystallisation processes as determined from DTA effects are summarised in Table 1.

ETA made it possible to study the microstructure development, especially on surface and subsurface regions during the heating of hydrated precursors of ruthenia–titania. A part of the ^{220}Rn atoms formed by the spontaneous α-decay of ^{224}Ra and trapped in the solid was released from the sample via diffusion, during the ETA measurements. The structural irregularities of solids served as diffusion paths for radon atoms. The increase in the radon release rate, *E*, indicated opening of the structure and/or the increase of surface area of the interfaces, whereas the decrease in *E* reflected the annealing of structure irregularities, serving as paths for radon migration, closing of pores and/or decrease in the surface area of the interfaces. These considerations are taken into account in the interpretation of ETA results [21] and will also be used for the comparison of ETA results with the results of other characterization methods used.

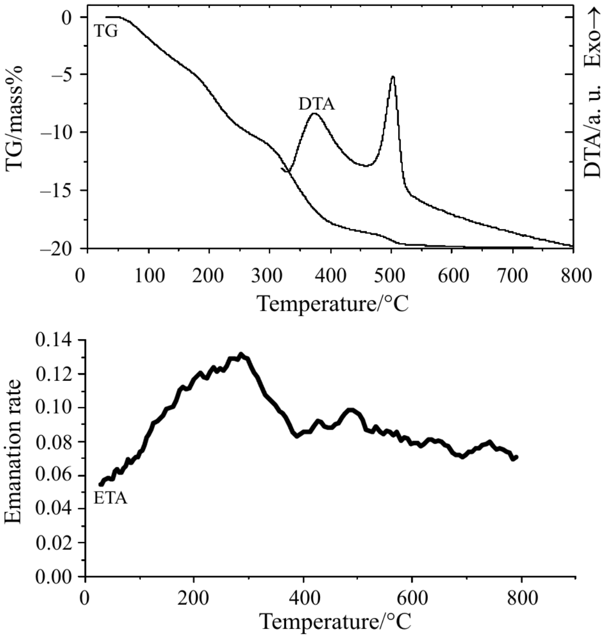

Fig. 7 TG, DTA and ETA results of hydrous precursors for ruthenia containing 50 mol% of titania

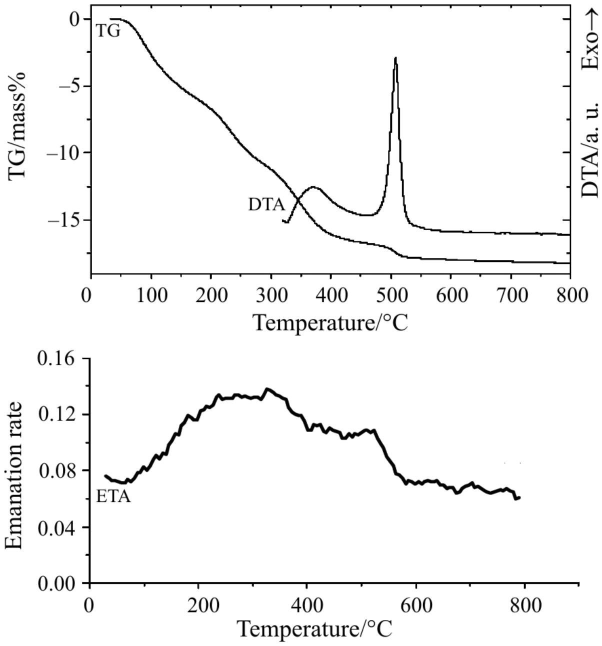

Fig. 8 TG, DTA and ETA results of hydrous precursors for ruthenia containing 70 mol% of titania

While comparing the ETA and DTA results (Figs 4–8) it followed that the ETA effects were observed at lower temperatures as compared to the respective DTA effects. We assumed that the enhanced radon release rate observed with all the investigated samples on heating above 100°C was due to the exposure of surface, initially covered by water molecules (ETA and DTA results in Figs 4–8). The newly formed fine grains and inter-boundaries of the fine particles agglomerates served as additional diffusion paths for radon release. On further heating above 250°C, the break observed on the ETA curves can be attributed to the ordering of sample structure due to the formation of crystalline phases. Temperatures of the break on ETA curves correspond to the onset of the structure ordering in the subsurface up to 60 nm, whereas the temperatures for maximal rate of *E* decrease were used as indicators of the maximal rate of the structure ordering, accompanied by the decrease of radon diffusion paths. The characteristic temperatures for the respective crystallisation processes as determined from the ETA

Table 2 ETA results of hydrated precursors of ruthenia-titania based materials

	Characteristic temperature/°C			
	1st crystallization process		2nd crystallization process	
Sample	onset of *E* decrease	maximum rate of *E* decrease	onset of *E* decrease	maximum rate of *E* decrease
Pure ruthenia	383	422	697	713
Ruthenia containing 10 mol% titania	345	430		
Ruthenia containing 30 mol% titania	300	321	442	469
Ruthenia containing 50 mol% titania	304	320	490	518
Ruthenia containing 70 mol% titania	250	381	506	543

curves are presented in Table 2. It should be pointed out that the break of ETA reflected the early stage of crystallization, in comparison to the DTA curve, which indicated the crystallization of the sample in bulk, observed at relatively higher temperature.

From the DTA results presented in Figs 4–8, it was inferred that the temperature of crystallization depends on the content of titania in the ruthenia–titania based samples. From the comparison of results obtained in this study and our previous studies [7, 8], it followed that the formation of two phases was dependent also on the atmosphere used during the heat treatment of the hydrous precursors. In addition, for $RuO_2 \cdot nH_2O$ the ETA results (Fig. 4) indicated the grain growth of ruthenia in the temperature range 650–780°C, which was also reflected in DTA as a small exothermic effect in the same temperature range (DTA curve Fig. 4). The enhanced radon release rate observed in the range 650–690°C was due to the migration of grain boundaries to the sample surface during the grain growth, whereas the subsequent decrease of *E* with the onset at 690°C reflected the decrease of the radon diffusion paths. This is in agreement with the SEM micrographs presented in our previous study [19] where the significant difference between the grain sizes was observed for the pure ruthenia samples heated to 500 and 800°C in argon. Moreover, it is also supported by the SEM micrographs presented in Fig. 9 in this study. It followed from Fig. 9a that the RuO_2

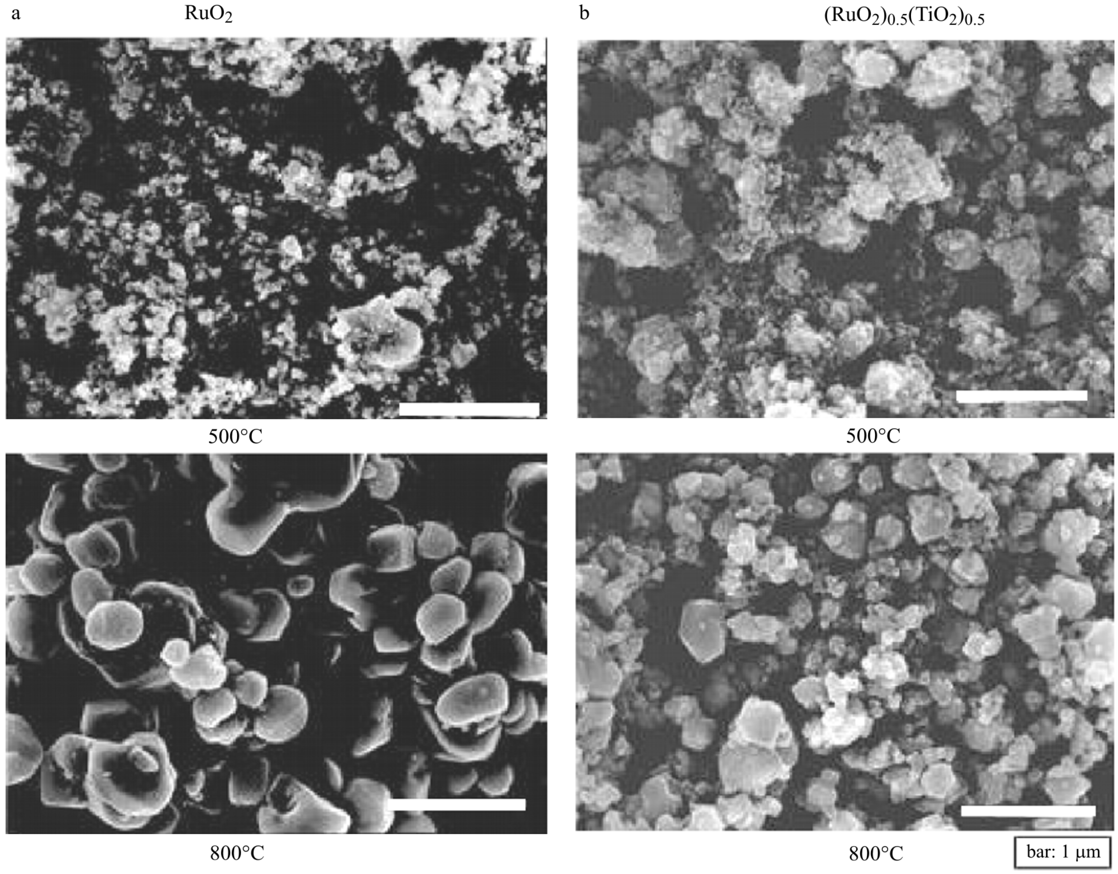

Fig. 9 SEM micrographs of the ruthenia based samples heated to 500 and 800°C a – RuO_2 and b – $(RuO_2)_{0.5}(TiO_2)_{0.5}$

heated to 500°C consists of the particle aggregates smaller than 0.05 μm, whereas significant grain growth was observed in the sample heated to 800°C in air, which is due to the particle sintering. However, much less sintering of the agglomerated grains was observed (Fig. 9b) for the sample $(RuO_2)_{0.5}$–$(TiO_2)_{0.5}$ heated to 800°C due to incorporation of ruthenia into titania. This is also in agreement with the ETA results of the latter sample (Fig. 7) where no significant effects were observed above 600°C that would correspond to the intense grain growth.

It should be pointed out that the ETA made it possible to characterize early stages of the solid state process, due to the fact that the surface and subsurface of the solid sample was labelled by radon to the depths of 60 nm.

Conclusions

Thermal behaviour of the hydroxide precursors of pure ruthenia and ruthenia containing various amounts of titania was studied using the methods of DTA, TG and ETA. The results were interpreted mainly with respect to the phase formation and crystallization of various ruthenia–titania phases including their possible solid solutions. It was demonstrated that the presence of the titania influenced the microstructure development of the precursors of ruthenia–titania based materials. The ETA brought about complementary information about the annealing of surface and subsurface layers in the respective temperature ranges. Temperatures of initial stages of the crystallization of respective phases were determined from ETA, while DTA characterized the crystallization of the samples in bulk. Possible formation of RuO_2–TiO_2 solid solution was observed in TG/DTA analysis as well as ETA. Although it was possible to confirm the presence of solid solution phase in XRD results of 50 mol% RuO_2–TiO_2 sample, it was difficult to identify such phases in other samples due to the overlapping of XRD peaks. It will be interesting to further characterize the wide range of RuO_2–TiO_2 type materials and work is in progress on structural characterization aspects.

The results obtained were helpful in the optimization of synthesis protocols for these materials to be used for the preparation of catalysts.The investigations of catalytic properties of the materials for NO_x decomposition and NO_x reduction are also in progress.

Acknowledgements

This study was supported in parts by the Grant from Science Agency of the Czech Republic (Project No. 104/04/0467), Ministry of Education of the Czech Republic (Project ME 497) and the Ministry of Education, Science, Culture and Technology (MEXT) of Japan. Development of catalytic materials for NO_x control is being carried out under the CSIR network project CORE-08(1.3). A part of this study was also carried out under the bilateral research cooperation between NEERI, India and NIMS Japan, while the characterization and evaluation studies were carried out in the frame of the research project based on the Scientific Cooperation between the Academy of Sciences of Czech Republic and CSIR India. Authors are also thankful to Dr. Arai and other scientists of Rigaku Denki Co. Japan for their help in analysis and interpretation of XRD data.

References

1 P. Baltzer, R. S. Davidson, A. C. Tseung, M. Graetzel and J. Kiwi, J. Am. Chem. Soc., 106 (1984) 1504.
2 G. Blondeel, A. Hariman, G. Porter, D. Urwin and J. Kiwi, J. Phys. Chem.-US., 7 (1983) 2629.
3 T. Kawai and T. Sakata, Chem. Phys. Lett., 72 (1980) 87.
4 N. K. Labhsetwar, A. Watanabe and T. Mitsuhashi, Appl. Catal. B, 40 (2003) 21.
5 H. Over and M. Muhler, Prog. Surf. Sci., 72 (2003) 3.
6 L. X. Yang, R. G. Allen, K. Scott, P. A. Christenson and A. Roy, Electrochim. Acta, 50 (2005) 1217.
7 J. Malek, A. Watanabe and T. Mitsuhashi, J. Therm. Anal. Cal., 60 (2000) 699.
8 V. Balek, T. Mitsuhashi, V. Zelenak, H. Haneda, J. Šubrt, E. Vecernikova and P. Bezdicka, J. Colloid Interface Sci., 248 (2002) 47.
9 V. Balek, Thermochim. Acta, 192 (1991) 1.
10 V. Balek and J. Tölgyessy, ‘Emanation thermal analysis and other radiometric emanation methods’, Comprehensive Analytical Chemistry, Part XII C, Ed. G. Svehla, Wilson and Wilson (Elsevier Sci. Publishers, Amsterdam 1984), p. 304.
11 V. Balek, J. Šubrt, T. Mitsuhashi, I. N. Beckman and K. Györyová, J. Therm. Anal. Cal., 67 (2002) 15.
12 F. Kovanda, V. Balek, V. Dornicak, P. Martinec, M. Maslan, L. Bilkova, D. Kolousek and I. M. Bountsewa, J. Therm. Anal. Cal., 71 (2003) 727.
13 V. Balek, J. Šubrt, J. Rouquerol, P. Llewellyn, V. Zelenak, I. M. Bountsewa, I. N. Beckman and K. Györyová, J. Therm. Anal. Cal., 71 (2003) 773.
14 V. Balek, Z. Malek, J. Šubrt, M. Guglielmi, P. Innozenzi, V. Rigato and G. Della Mea, J. Therm. Anal. Cal., 76 (2004) 43.
15 V. Balek, T. Mitsuhashi, J. Šubrt, S. Barardijeva and Z. Malek, J. Therm. Anal. Cal., 72 (2003) 119.
16 L. A. Perez-Maqueda, V. Balek, J. Poyato, J. L. Perez-Rodriquez, I. M. Bountsewa, I. N. Beckman and Z. Malek, J. Therm. Anal. Cal., 71 (2003) 715.
17 J. F. Ziegler and J. P. Biersack, The stopping and range of ions in solids, Pergamon Press, New York 1985.
18 J. Malek, A. Watanabe and T. Mitsuhashi, Thermochim. Acta, 282/283 (1996) 131.
19 T. Mitsuhashi, A. Watanabe, V. Balek, E. Klosová, J. Málek, J. Šubrt and V. Štengl, Mater. Lett., 39 (1999) 46.
20 T. Terasaka, M. Sc. Thesis, Waseda University Tokyo, 2002.
21 V. Balek, T. Mitsuhashi, J. Šubrt, P. Bezdicka and J. Fusek, J. Therm. Anal. Cal., 60 (2000) 691.