Study of the preparation of ruthenia based catalytic materials by heating their precursors

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Thermal behaviour of hydrous ruthenia ($RuO_2 \cdot nH_2O$) and ruthenia containing 10% titania (($(RuO_2)_{0.9}-(TiO_2)_{0.1} \cdot nH_2O$) was characterised on heating in air by emanation thermal analysis (ETA), thermogravimetry (TG), differential thermal analysis (DTA) and evolved gas analysis (EGA). The anhydrous ruthenia and ruthenia containing 10% titania samples were prepared by heating their hydrous precursors at 500°C in air. The temperature intervals of the samples dehydration and crystallisation were determined. XRD, TEM and surface area measurements were also used for the characterisation of the samples. The ETA results, evaluated by a mathematical model, brought about new information about surface area and microstructure development of the intermediate products of the oxides under *in situ* conditions of the heating in air. A good agreement between ETA and the results of other methods was obtained. The NO_x reduction by CO was used to test the catalytic properties of these samples. © *2004 Kluwer Academic Publishers*

1. Introduction

The ruthenium oxide has been proposed as catalyst for several catalytic reactions of technological and environmental importance [1–3]. Thermal treatment of ruthenia based hydrous oxides was investigated with the aim to determine optimal conditions of their heat treatment and to prepare ruthenia based catalysts [4, 5]. As it was already demonstrated in our previous studies, thermal treatment of hydrous oxides in argon gave rise to the crystalline (rutile based) product [6–10]. In this study we used the air heating of ruthenia based hydrous oxide to prepare catalysts for NO_x reduction. Thermogravimetry (TG), differential thermal analysis (DTA), evolved gas analysis (EGA) and emanation thermal analysis (ETA) were used in order to elucidate the processes during the preparation of pure RuO_2 and RuO_2 containing 10% TiO_2. Products of thermal treatment of the precursors were characterised by surface area measurements (BET), transmission electron microscopy (TEM) and X-ray diffraction (XRD). The NO_x reduction by CO was used to test the catalytic

properties of the samples prepared by heating in air at 500°C for one hour.

2. Experimental section

2.1. Samples preparation

Reagent grade $RuCl_3 \cdot nH_2O$ (Furuya Metal) and $TiCl_4$ (Kanto Chemicals) were used as starting materials. Ruthenium chloride solution was prepared by dissolving $RuCl_3 \cdot nH_2O$ in 0.1 N 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 solutions were added dropwise to 2 N aqueous ammonia solution. The precipitates obtained were washed, filtered and dried at 120°C. The resulting hydrous precursors of ruthenia ($RuO_2 \cdot nH_2O$) and ruthenia containing 10% titania (($(RuO_2)_{0.9}$-$(TiO_2)_{0.1} \cdot nH_2O$) were used for the preparation of anhydrous samples and for the ETA, TG, DTA and EGA measurements. The catalytic materials i.e., the anhydrous oxides samples, RuO_2 and

RuO_2 containing 10% TiO_2, were prepared by heating the respective hydrous precursors, namely $RuO_2 \cdot nH_2O$ and $(RuO_2)_{0.9}$-$(TiO_2)_{0.1} \cdot nH_2O$ in air at 500°C 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 solution of their nitrates. Immediately after the labelling, the acetone was evaporated at approximately 40°C. The specific activity of the labelled sample was 10^5 Bq per gram.

2.2. Methods used

The emanation thermal analysis (ETA), based on the measurement of radon release rate from the samples previously labelled, has been described in [11, 12]. As it follows from [12, 13] the increase in radon release rate, E, measured during ETA, can be ascribed to the opening of the structure and/or to the increase of surface area of interfaces, whereas the decrease in E reflects the annealing of structure irregularities that served as paths for radon migration, the closing of pores and/or the decrease in the surface area of interfaces. It was determined by means of TRIM code [14] that the maximum depth of the labelling by [224]Ra and [220]Rn recoiled atoms in the ruthenia based materials was 80 nm.

The catalytic activity measurements were carried out using a pure gas steady state, laboratory assembly equipped with precise gas flow control and heating system. Gas analysis was carried out using an auto-sampling PC controlled gas chromatograph. The catalyst samples tested in the form of pellets and a thermal pre-treatment was used to desorb the gases, by flowing He over the catalyst, at 300°C for 3 h. The pellets of approximately 20–40 mesh were prepared by applying pressure of 300 kgf/cm^2.

A feed gas mixture with the following composition was allowed to flow over the catalyst: NO (1000 ppm) + CO (1000 ppm) + balance He. The ratio of sample weight to gas flow (space velocity) used for the reaction was approximately 0.15 g·s·/N·cm^{-3}. The catalytic reaction for NO reduction was investigated with the samples after the thermal pre-treatment. The catalyst was first stabilised at 300°C with the flowing feed gas mixture for 2 h and subsequently the concentration of resulting reaction products (N_2 and CO_2) were determined using gas chromatograph. The catalytic
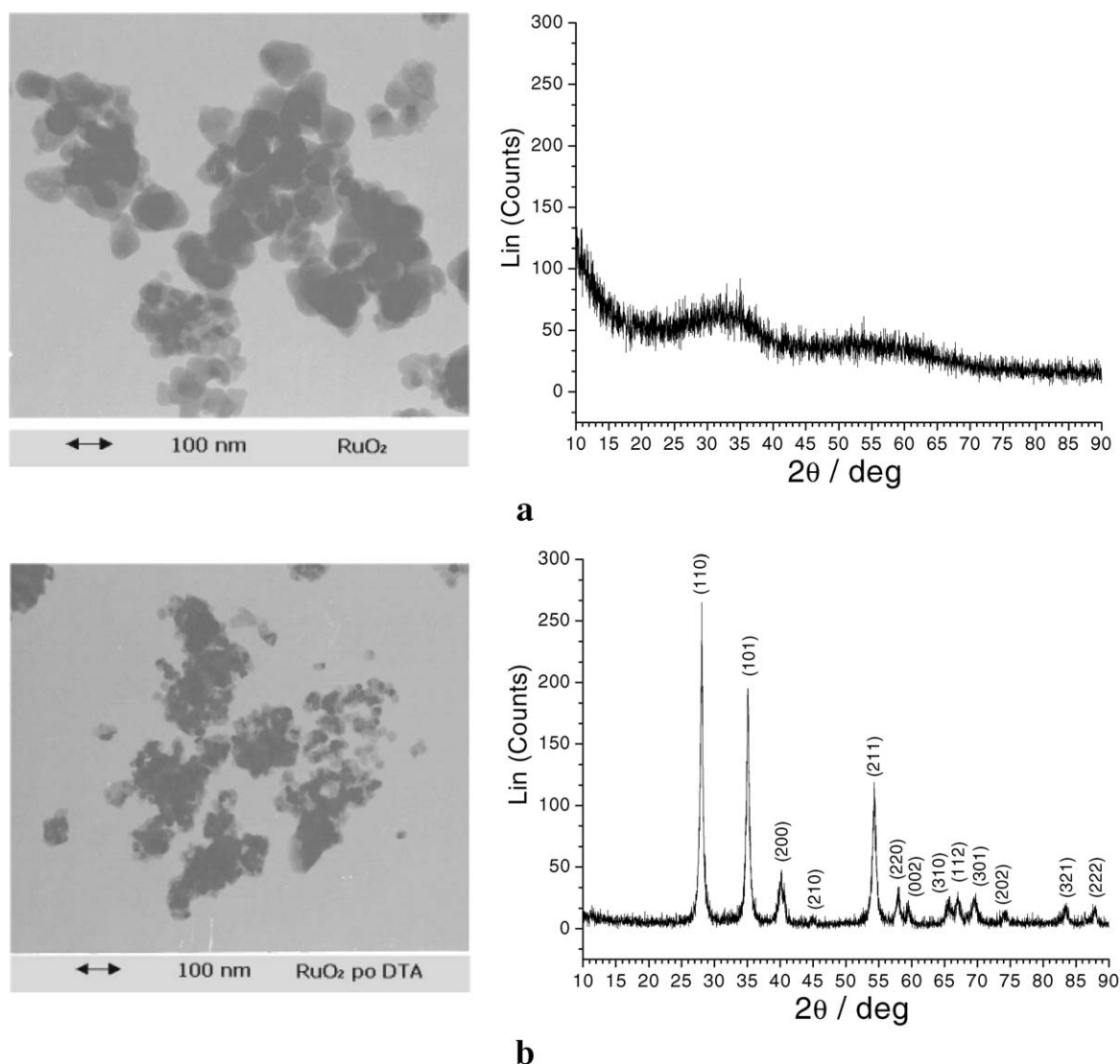

Figure 1 TEM micrographs and XRD patterns of: (a) initial hydrous ruthenia and (b) anhydrous ruthenia prepared after heating at 500°C for one hour in air.
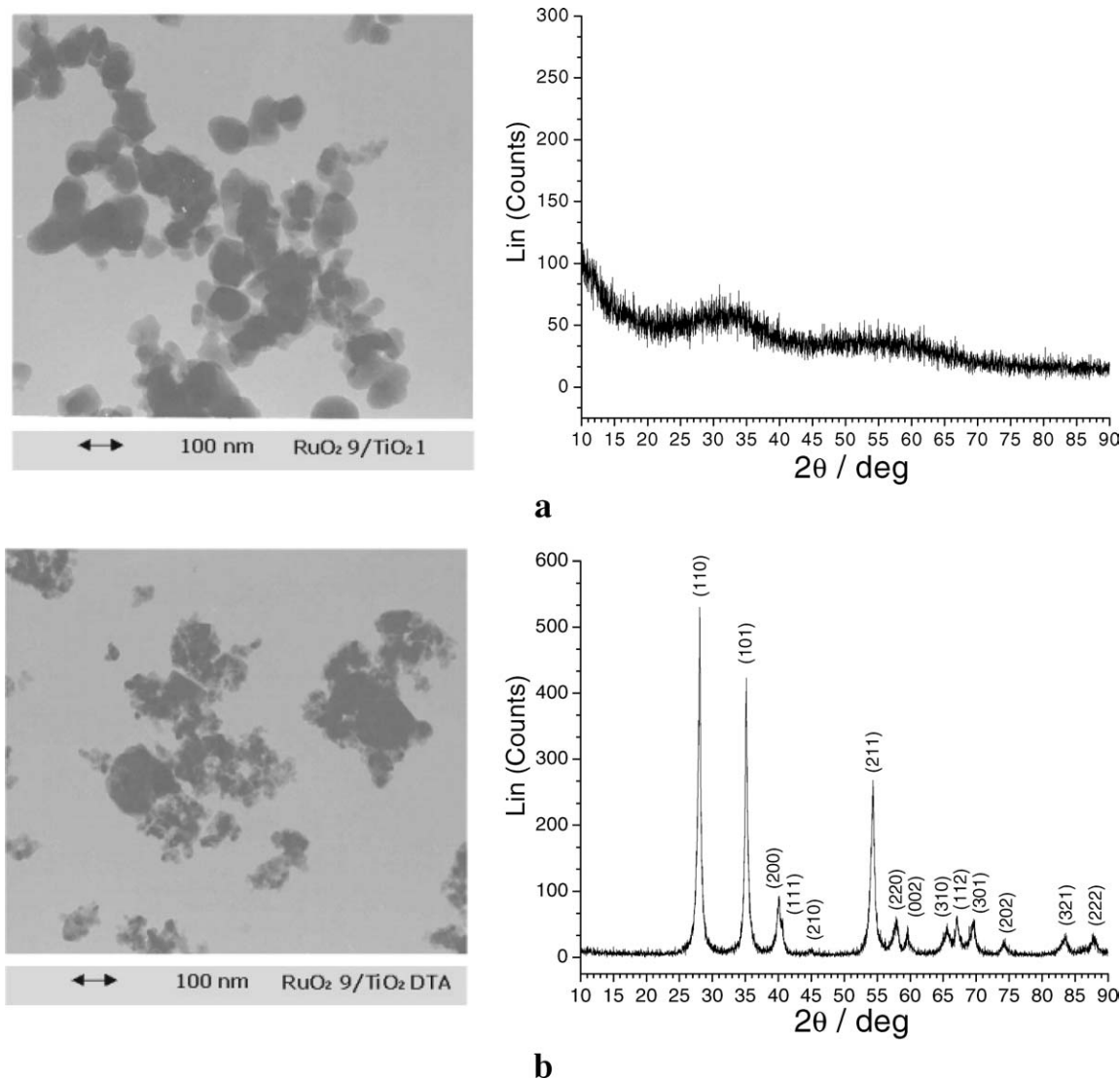
Figure 2 TEM micrographs and XRD patterns of: (a) initial hydrous ruthenia containing 10% titania and (b) anhydrous ruthenia containing 10% titania prepared after heating at 500°C for one hour in air.

activity for NO reduction by CO was derived from the gas analysis data for N_2 and CO_2 in the reaction products.

2.3. Equipments and conditions used for samples characterisation

The NETZSCH DTA–ETA 404 Apparatus was used for the ETA measurements. The samples amount of 0.05 gram placed into corundum crucibles was during the ETA measurements overflowed by the constant flow of air (50 cm³/min), which carried the radon released from the sample into the measuring chamber of radon radioactivity.

DTA/TG/EGA measurements were carried out using NETZSCH STA 409 Apparatus equipped with quadrupole-type mass spectrometer BALZERS (the ion mass of $m/z = 18$ was used for water molecules determination). The samples amount of about 0.05 g, corundum crucibles and heating in air at the rate of 6 K/min were used for the DTA/TG/EGA measurements.

XRD patterns were recorded with a PHILIPS diffractometer using Cu K_α Ni-filtered radiation. TEM micrographs were obtained by TESLA BS 500 equipment. Surface area was measured by nitrogen adsorption using the automatic gas adsorption apparatus BELSORP 28SA (produced by Nippon Bell Co.) and evaluated by B.E.T. method.

Catalytic activity measurements were carried out by using the laboratory apparatus R8300 (Okura Riken Ltd. Co. Japan), equipped with the gas chromatograph MTI-P-200.

3. Results and discussion

3.1. Characterisation of the samples

The hydrous ruthenia and ruthenia-titania samples were investigated by means of TEM, XRD, TG/DTG, DTA, EGA with MS detection, emanation thermal analysis (ETA) and surface area measurements using nitrogen adsorption.

From TEM micrographs and XRD patterns (see Fig. 1a) it followed that the grains of hydrous ruthenia were of irregular shape of the size 70–100 nm and amorphous. After heating the hydrous ruthenia in air at 500°C for one hour the sample size diminished to 20–50 nm, nevertheless larger agglomerates of the size
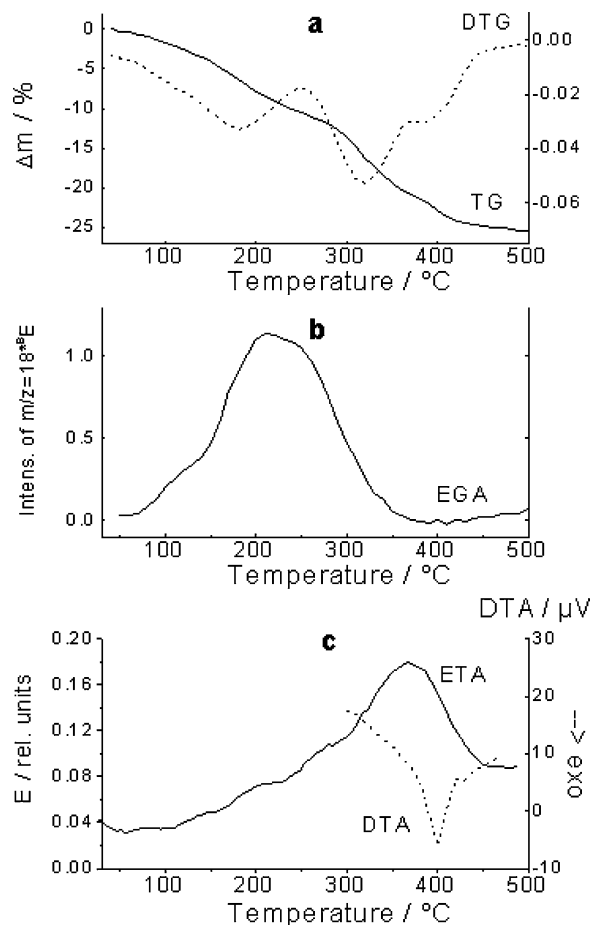
Figure 3 Results of: (a) TG/DTG, (b) EGA DTA and (c) ETA for hydrous ruthenia sample measured during heating in air at the rate 6 K/min.

around 100 nm were observed. The sample became crystalline of rutile structure (PDF:40-1290) (see Fig. 1b).

Similarly, from TEM micrographs and XRD patterns of the hydrous ruthenia containing 10% titania (see Fig. 2a) it followed that the grains were of irregular shape of the size 60–100 nm and amorphous. From the TEM micrographs presented in Fig. 2b it is obvious that

after heating the sample in air at 500°C for one hour the size of grains decreased to 30–50 nm, however agglomerates of the size around 100 nm were observed. Moreover, from Fig. 2b it followed that after heating to this temperature the initial sample became crystalline of rutile structure (PDF:40-1290). This is in agreement with the previous finding [9] that $(RuO_2)_{0.9}$-$(TiO_2)_{0.1}$ sample represents a rutile structure solid solution.

In order to characterise the dehydration and microstructure development on heating of the samples used as precursors for the ruthenia-based catalysts hydrous ruthenia and ruthenia containing 10% titania were investigated by thermogravimetry (TG), differential thermal analysis (DTA), evolved gas analysis (EGA) and emanation thermal analysis (ETA).

3.2. Thermal behaviour of hydrous ruthenia
The TG/DTG curves of the hydrous ruthenia sample $(RuO_2 \cdot nH_2O)$ measured during heating in air are presented in Fig. 3a. The mass loss observed in the range 50–500°C was due to the dehydration of the sample, as confirmed by EGA (see Fig. 3b), where the release of water is represented in the mass spectrum by ions with $m/z = 18$. The dehydration of the hydrous ruthenia took place in three steps, namely: 50–260°C, $260 - 380°C$, and 380–500°C. The last step of the dehydration was accompanied by the crystallisation indicated by the DTA exothermic effect at 400°C (see Fig. 3c). The microstructure development, which accompanied the dehydration of the $RuO_2 \cdot nH_2O$ sample, was characterised by ETA (see Fig. 3c) on heating under identical conditions as were used for the TG, EGA and DTA measurements.

The enhanced radon release rate with onset at 70°C reflected the exposure of sample surface, initially covered by water molecules. We assumed that at the early stage of the sample crystallisation the inter-boundaries of the surface of the newly formed fine grains served as additional diffusion paths for radon release, which was characterised by the enhanced radon release rate
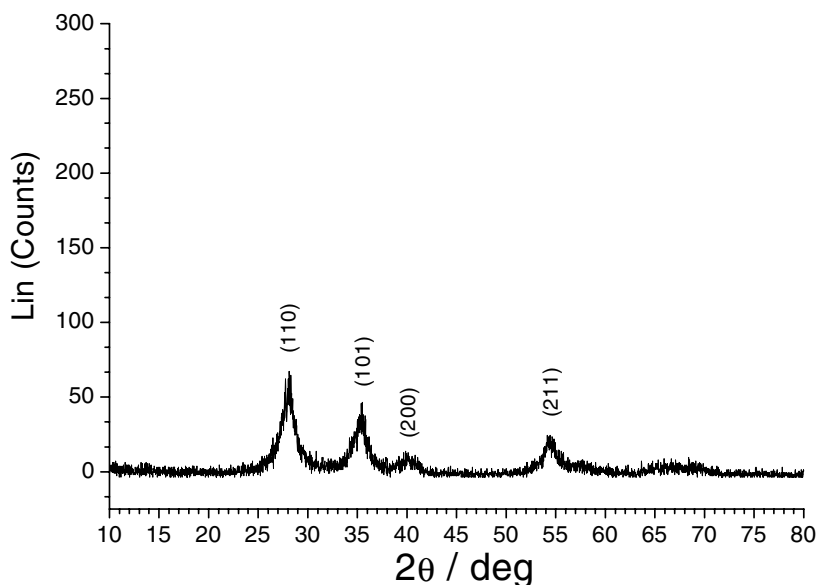

Figure 4 XRD pattern of hydrous ruthenia sample prepared by heating to 330°C in air and subsequent cooling to room temperature.

E, from the sample on heating above 320°C. In order to characterise the structure of the intermediate product of crystallisation, the initial sample of hydrous ruthenia heated to 330°C in air, was examined by XRD. From the XRD pattern of this sample (see Fig. 4) it followed that a partially (poorly) crystalline ruthenia was obtained after heating to 330°C.

From the ETA curve presented in Fig. 3c we were able to determine the temperature (380°C) at which the intense crystallisation of the sample took place. This temperature corresponds to the break observed on the ETA curve (Fig. 3c). The following decrease of the radon release rate, E, was ascribed to the ordering of the sample structure, which caused the decrease of the number of radon diffusion paths. This is in agreement with the XRD results presented in Fig. 1b, demonstrating that in the sample heated at 500°C a well crystalline ruthenia was detected.

3.3. Thermal behaviour of hydrous ruthenia containing 10% titania

From TG/DTG curves in Fig. 5a it followed that the dehydration of the hydrous ruthenia containing 10% titania took place in three steps similarly as with the hydrous ruthenia, namely: 50–260°C, 260–380°C, and 380–500°C. The water release in first two steps was
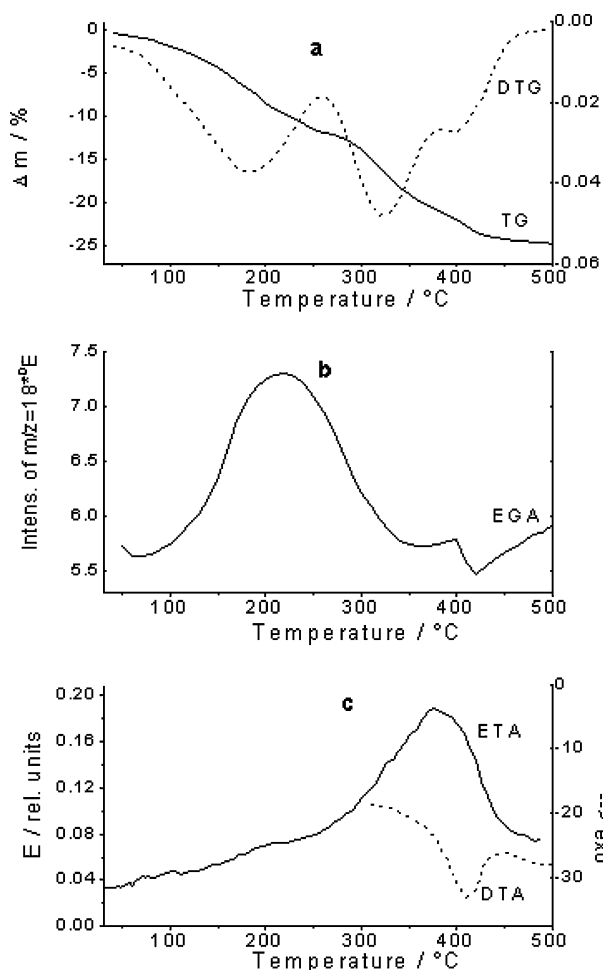
indicated also by EGA (see Fig. 5b), in the range from 70 to 360°C. The last step of the dehydration was accompanied by the crystallisation indicated by DTA exothermic effect at 411°C for the sample of ruthenia, containing 10% titania with the proposed formula sample $(RuO_2)_{0.9}$-$(TiO_2)_{0.1} \cdot nH_2O$ (see Fig. 5c).

From the ETA results (see Fig. 5c) it followed that the similar microstructure development took place on heating with the $(RuO_2)_{0.9}$-$(TiO_2)_{0.1} \cdot nH_2O$ as with the $RuO_2 \cdot nH_2O$ sample (see Fig. 3c). The enhanced radon release rate starting at 70°C reflected the exposure of surface, initially covered by water molecules. We assumed that at the early stage of the sample crystallisation the inter-boundaries of the newly formed fine grains served as additional diffusion paths for radon release, which was observed as the enhanced radon release rate E, from the sample on heating above 330°C. The increase of E was interrupted at 390°C and turned to the decrease of E to be ascribed to the ordering of the sample structure and formation of rutile type lattice, as confirmed by XRD patterns presented in Fig. 2b. The crystallisation of the sample was indicated by the DTA exothermal effect observed at 411°C (Fig. 5c).

It should be pointed out that the emanation thermal analysis was reflecting the process of the early stage of crystallisation, in comparison to the DTA curve, which indicated the crystallisation of the sample in bulk. The temperature of the break of the radon release rate observed at approximately 380°C for both $RuO_2 \cdot nH_2O$ and $(RuO_2)_{0.9}$-$(TiO_2)_{0.1} \cdot nH_2O$ samples, respectively, was about 20°C lower than the DTA peak temperature. (For the ETA and DTA curves see Figs 3c and 5c). This confirmed our assumption that the ETA reflected the processes, taking place in the subsurface layers of the sample and the early stage of crystallisation.

3.4. Recommendation of conditions for the ruthenia–based catalytic materials preparation

For both hydrous ruthenia and ruthenia-tiania samples additional ETA measurements were carried out on isothermal heating in air at 500°C for two hours. From the ETA results presented in Fig. 6, it follows that a steeper decrease of the radon release
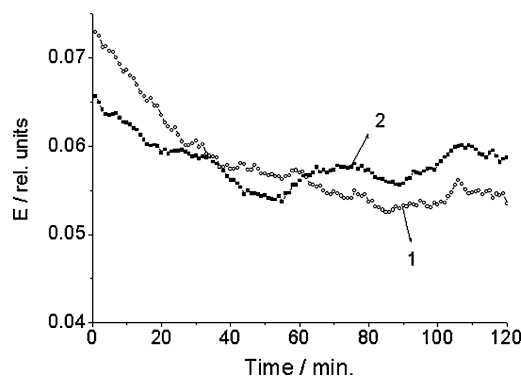

Figure 5 Results of: (a) TG/DTG, (b) EGA DTA and (c) ETA for hydrous ruthenia containing 10% titania sample measured during heating in air at the rate 6 K/min.

Figure 6 Time dependencies of the radon release rate measured during isothermal heating of samples at 500°C for 2 h in air; curve 1-pure ruthenia, curve 2-ruthenia containing 10% titania.

rate, E, was observed during this isothermal heating for pure RuO_2(curve 1, Fig. 6) than for $(RuO_2)_{0.9}$-$(TiO_2)_{0.1}$(curve 2, Fig. 6). The differences in the time dependence of radon release rate, E, observed on isothermal heating of the samples were ascribed to the surface and subsurface microstructure annealing. A higher tendency to the annealing was observed with pure RuO_2 as compared to $(RuO_2)_{0.9}$-$(TiO_2)_{0.1}$. As after one hour of the isothermal treatment at $500°C$ the decrease of the E values remained constant, it was recommended from the ETA results that the one hour heating at $500°C$ are optimal conditions for the preparation of the ruthenia-based catalytic materials investigated in this study. The surface area values S determined by B.E.T. method after heating of the samples at $500°C$ for one hour were $S = 24.4\,m^2/g$, for RuO_2 and $S = 29.36$ m^2/g for $(RuO_2)_{0.9}$-$(TiO_2)_{0.1}$.

It is worthy to mention the differences in the crystallinity of the ruthenia based materials prepared by thermal treatment at $500°C$ in air and argon respectively. In our previous studies [6, 7] poorly crystalline

RuO_2 and $(RuO_2)_{0.9}$-$(TiO_2)_{0.1}$ were prepared by heating of hydrous ruthenia and ruthenia-titania in argon to $500°C$. On the contrary, well crystalline samples were obtained in this study by heating of the same hydrous precursors in air (for the respective XRD patterns see Figs 1b and 2b).

3.5. Mathematical modelling and evaluation of ETA results

In order to characterise more precisely the differences in the microstructure development of ruthenia based catalytic materials prepared in this study, the ETA results were evaluated using mathematical model proposed by Beckman and Balek [15]. It was supposed in the modelling that ^{228}Th and ^{224}Ra do not migrate in the solid at the temperatures used for the ETA measurements. The microstructure changes, that resulted in the annealing of the radon diffusion paths (channels) in the samples of ruthenia and ruthenia containing 10% of titania, were described by the function $\Psi(T)$. The
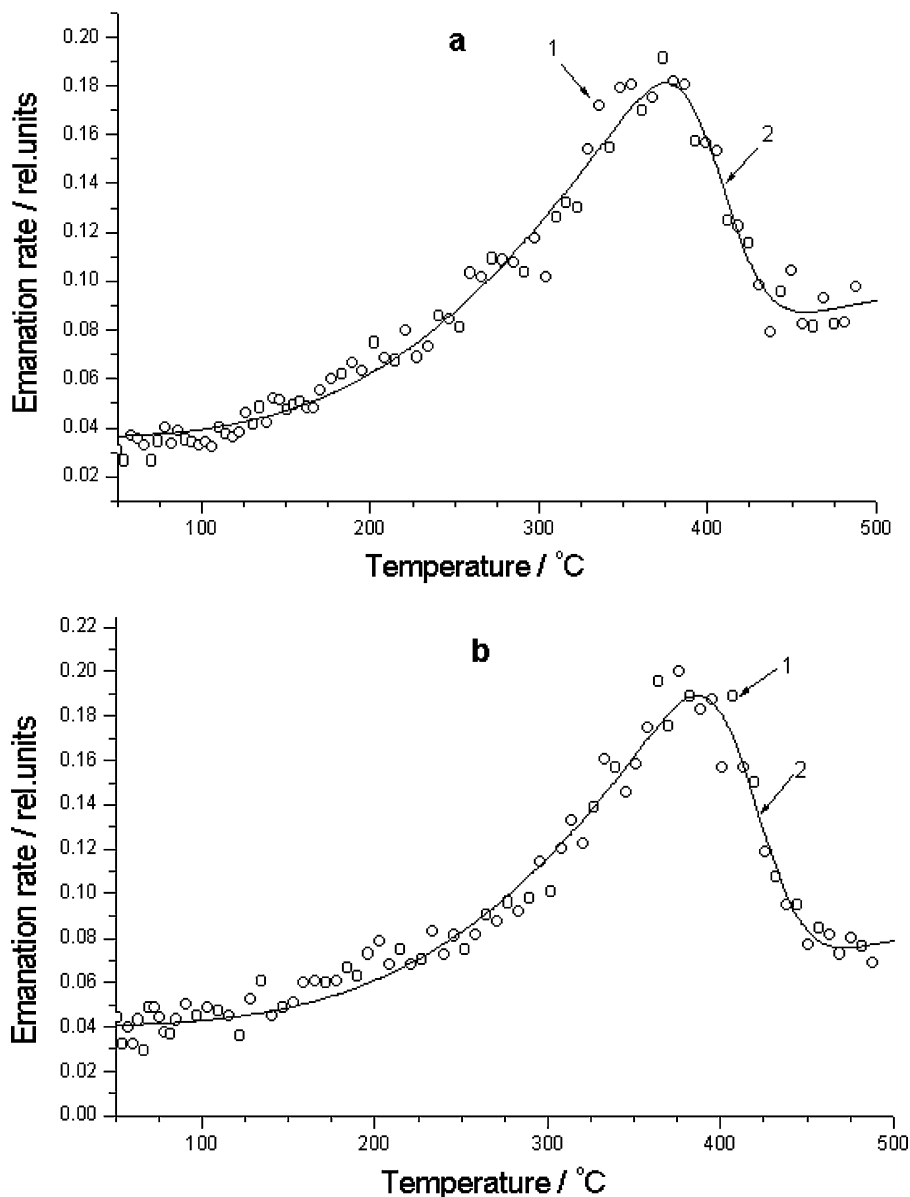
Figure 7 Experimental ETA results (points-circles) and temperature dependencies $E(T)$ of radon release rate obtained by modelling (full lines) characterizing: (a) $RuO_2 \cdot nH_2O$ and (b) $(RuO_2)_{0.9}$-$(TiO_2)_{0.1} \cdot nH_2O$ samples.

temperature dependence of the emanating rate, $E(T)$, can be schematically written

$$E(T) = E_D(T) \cdot \Psi(T) \qquad (1)$$

where E_D characterises the radon permeability of diffusion channels, and the $\Psi(T)$ characterises the changes of the structural irregularities, which served as channels for radon diffusion in the samples. Following expressions for $E_D(T)$ and $\Psi(T)$ were used in the present study:

$$E_D(T) = p1 \cdot p2 \cdot \exp\left(-\frac{p3}{T}\right)$$

$$\cdot \left[\coth\left(\frac{3}{p1 \cdot \exp(-\frac{p3}{T})}\right) - \frac{p1 \cdot \exp\left(-\frac{p3}{T}\right)}{3}\right]$$

$$(2)$$

and

$$\Psi(T) = 1 - \frac{p4}{2}\left[1 + \mathrm{erf}\left(\frac{T - p5}{\sqrt{2 * p6}}\right)\right] \qquad (3)$$

where $p1$–$p6$ are parameters used in the fitting of the model curve with the ETA experimental results. During the calculation of these parameters, we assumed that the processes of dehydration and crystallisation can be described by formal first order kinetics.

Fig. 7a and b depict the experimental ETA results for ruthenia and ruthenia-titania samples respectively. Curve 1 (circles) corresponds to the experimental values of temperature dependencies $E(T)$ of radon release rate, and curve 2, (full line) correspond to the to the temperature dependencies obtained by modelling. The respective $\Psi(T)$ functions, which were used in the mathematical model and their first derivatives $d\Psi/dT$ are presented in Fig. 8. The $\Psi(T)$ functions characterised the microstructure changes, which caused the annealing of radon diffusion paths in the ruthenia and ruthenia-titania samples. Following values of T_{max}, (which indicate temperatures of maximal crystallisation rate of the samples) were determined from the derivative functions $d\Psi/dT$, namely: $T_{max} = 402°C$ for the ruthenia sample and $415°C$ for the ruthenia-titania sample. From Fig. 8 it follows, that T_{max} value, which characterised the crystallisation, was found higher for $(RuO_2)_{0.9}$-$(TiO_2)_{0.1}$ in comparison to pure RuO_2.

From the parameters $p3$ and $p5$ obtained by modelling, the activation energy Q_D (kJ·mol^{-1}) of radon diffusion as well as enthalpy ΔH (kJ·mol^{-1}) of the crystallisation were calculated using Equations 4 and 5.

$$Q_D = 2 \cdot \boldsymbol{R} p3 \, (\mathrm{kJ} \cdot \mathrm{mol}^{-1}) \qquad (4)$$

where $\boldsymbol{R}$ is gas constant

$$\Delta H(T) = T_{max}^* \left[69.5 + 4.6 * \log_{10}\left(\frac{T_{max}}{\beta}\right)\right]$$

$$(\mathrm{kJ} \cdot \mathrm{mol}^{-1}) \qquad (5)$$

where, $T_{max} = p5$ is the temperature of maximal rate of the crystallisation and β is the heating rate used in ETA experiments. The calculated values of the activation
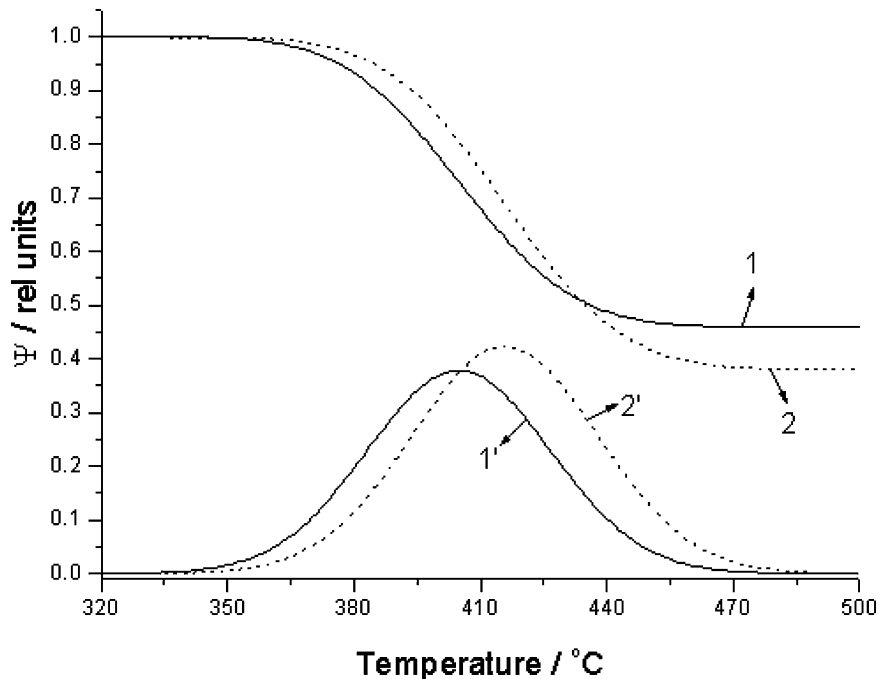

Figure 8 Temperature dependencies of $\Psi(T)$ functions and $\Psi(T)/dT$ derivative functions compared to the DTA curves for $RuO_2 \cdot n H_2O$ and $(RuO_2)_{0.9}$-$(TiO_2)_{0.1} \cdot n H_2O$ samples. Curves 1 and 2 represent the corresponding $\Psi(T)$ functions and curves 1' and 2' represent the corresponding $\Psi(T)/dT$ derivative functions.
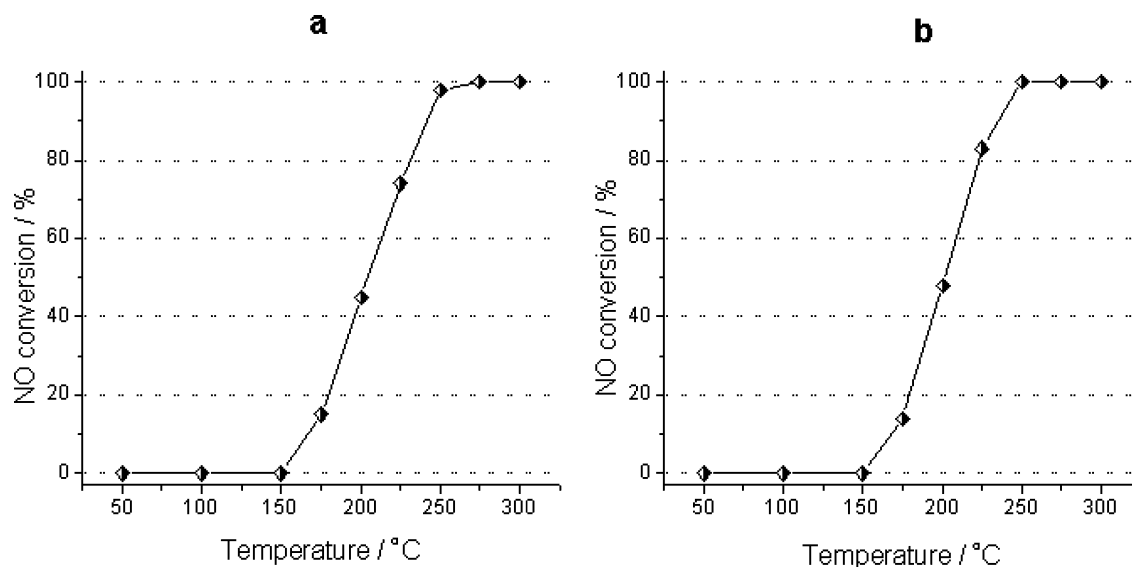
Figure 9 Catalytic activity of: (a) RuO_2 and (b) $(RuO_2)_{0.9}$-$(TiO_2)_{0.1}$ tested using the reduction reaction $NO + CO \rightarrow N_2 + CO_2$.

energy Q_D of radon diffusion and the enthalpy ΔH of the crystallisation were as follows: for pure ruthenia sample $Q_D = 57.2$ and $\Delta H = 50.8$ kJ·mol^{-1}, and for ruthenia-10%titania sample $Q_D = 60.0$ and $\Delta H = 54.4$ kJ·mol^{-1}.

3.6. Catalytic evaluation studies

Results of the catalytic evaluation of ruthenia–based samples are presented in Fig. 9. Both samples of ruthenia–based catalysts prepared on heating of hydrous precursors in air showed reasonably good catalytic activity for NO_x reduction by CO and almost 100% conversion was observed at 250°C. The catalytic activity of ruthenia containing 10% titania was found slightly higher than that of pure ruthenia sample. This could be due to the synergy effect or surface area changes, which took place during preparation of the samples (for ETA results see Figs 3c and 5c). There was practically no change in the catalytic activity even after continuous run lasting more than 12 h, thereby showing stability of catalyst and its non-reactivity with the feed gas used. The used catalytic materials were also checked by XRD for any structural changes. However, practically no change was observed in both the materials even after the prolonged exposure to the reaction mixture.

4. Conclusions

ETA was found suitable in the characterisation of microstructure changes during the formation of ruthenia based catalytic materials from their precursors. A good agreement among the ETA, TG, DTA, and EGA results was observed. The ETA provided additional information on changes in surface and subsurface layers under *in-situ* conditions of heating of these materials and their intermediate products. The mathematical model proposed and used for the first time in this study was found suitable for the evaluation of the ETA results that fitted well with the model curves. Based on the ETA re-

sults, the heating of hydrous precursors in air at 500°C for one hour was recommended for the preparation of ruthenia based powders to be further studied as catalyst for NO_x reduction reaction. ETA can be useful as a complementary technique to other characterisation methods for optimisation and standardisation of synthesis protocols for various catalytic materials with desired surface properties. Both ruthenia and ruthenia-10% titania prepared in this study show good catalytic activity for NO_x reduction.

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