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# Application of radioactive inert gases for the investigation of heterogeneous catalysts and other solids

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## Abstract

The possible applications of the emanation method, when radioactive inert gases are used to label the surface under study, are considered. Examples are given of the application of the method to the study of the processes of catalyst preparation, solid phase transitions and for investigating the heterogeneous catalytic reaction of isopropanoldehydration (dehydrogenation) over alumina and titanium oxide based catalysts. It is shown that the method can be used to determine the solid phase transition features including phase transitions without heat effects and allows the temperature region of the transitions and their kinetic parameters and the range of activation energies to be established. The method can be used to investigate heterogeneous catalytic reactions directly in the course of catalysis in order to obtain information about the local interaction of the reagent with the catalytic surface, the region of the catalytic action and the changes in the type of catalytic sites and the route of reaction Particularly valuable information can be obtained by combining the emanation method with other physico-chemical techniques, e g. X-ray phase analysis, differential thermoanalysis, dilatometric analysis and thermogravimetric analysis.

## INTRODUCTION

In recent years the need to find a means of investigating directly the changes that occur on the surface and in the bulk of a catalyst in the course of heterogeneous catalytic reactions has become a high priority. This is one of the reasons for the development of in situ physico-chemical methods in heterogeneous catalytic investigations which allow the changes that occur in the catalyst phase composition, structure and surface condition during the catalytic process to be recorded. Such methods include X-ray phase analysis using a small volume, high temperature gas-flow chamber [1], Mössbauer

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spectroscopy [2], electron paramagnetic resonance [3,4], NMR [5], and Extended X-ray Absorption Fine Structure (EXAFS) [6]. The development of these methods has been possible due to the creation of highly efficient experimental techniques. The more sensitive radiometric emanation method was used by Zhabrova et al. [7] as long ago as the 1950s and 1960s.

The emanation method is based on the introduction into solids of radioactive inert gases followed by the measurement of the emanation release fraction. The release of emanation allows the temperature and the time of the catalyst transformation from one state to another to be determined directly during the course of the catalytic process.

The classical emanation method which employs radioactive gases of natural origin was first proposed by Kolovrat-Chervinskii [8] and was developed further by Hahn [9], Zimens [10] and Starik [11]. Today different variations of this method are known which are based on the application of artificial radioactive isotopes of inert gases [12–14]. The range of problems that can be investigated by emanation methods is expanded in many cases by their use in combination with X-ray structure, thermographic, dilatometric and sorption methods. Such combinations of methods enable more reliable explanations of the observed phenomena to be proposed [15]. The theoretical and practical aspects of the emanation techniques have been recently reviewed [16].

## MAIN FEATURES OF THE EMANATION METHOD

The total emanating power (usually designated as $E$) of a sample consists of two parts: $E_R$ and $E_D$. According to emanation theory [17], $E_R$ and $E_D$ correspond to two different mechanisms of atom emanation release: the fraction of atoms which release directly due to the recoil energy of the radioactive decay of the mother radioelement ($E_R$); and the emanation atoms created inside the solids and their release by diffusion through vacancy clusters, capillaries and cracks in solids ($E_D$). The recoil atom is only released from a particle when the mother element is located at a distance $x$ which does not exceed the recoil run $R$. A comparison of the calculated and experimentally determined energy and run values for the recoil emanation atoms, derived from the equations given in refs. 17 and 18, has been reported [18]. It should be noted that theoretically calculated values of the average value of the recoil run are in satisfactory agreement with the experimentally determined ones although not for all systems, so that in investigations where the emanation method is used the results obtained can be interpreted semiquantitatively or can be supplemented by data obtained by means of other methods.

In considering the emanation process in particle clusters, it is also necessary to take into account the effect of the recoil of random action which arises on collision of the recoil atom with a neighbouring particle of the solid. The gaps between particles of less than 1 $\mu$m in diameter are, as a rule, not more than the length of the recoil path and the emanation atoms release mainly due to the recoil of undirected action. The fraction of emanation atoms is a sensitive function of the composition of the solid and the presence of impurities [19]. If it is assumed that all recoil atoms are released just after their creation and that the rate of release does not depend on the quantity of inert gases present in the sample, then the emanating power of a freshly prepared sample is practically due only to the recoil effect. The diffusion component of emanation is a function of the total concentration of the gas and the age and the temperature of the sample.

The choice of incorporation technique and the distribution of mother elements in the solid under investigation is of great importance in the emanation method. For most sediments having a high specific surface, a uniform distribution of radioelements is possible even in the absence of isomorphism [10]. There are several types of ETA measurements: the measurement of the emanating power ($E$) under continuous heating of the sample; the measurement of $E$ after interruption of heating at a given point and cooling of the sample; the measurement of $E$ under isothermal conditions; and the measurement of $E$ directly during the cooling of a sample previously heated to a high temperature. There are several different ETA techniques which differ mainly in the technique used to incorporate the radioactive inert gas into the solid under investigation. What is common to these methods is that gas emanates only by diffusion and is not enriched. In connection with this, it is necessary to take into consideration its decay over time.

One of the most interesting versions of the classical emanation method is the surface gas labelling method which is based on incorporating radioactive radon, xenon or krypton ($^{131}$Xe or $^{85}$Kr) into thin surface layers by ion bombardment of a solid surface by means of a high-frequency discharge [12]. This surface labelling method can be used to determine the topography of different surface structures, to observe the surface reaction course, and to investigate the dependence of the diffusion mechanism of inert gases in oxides and metals on the preliminary treatment of their surface, which is of special interest in the investigation of catalytically active solids [20,21].

Other techniques for incorporating the inert gas [14,22] involve introducing the inert-gas atoms into the surface of a solid by using the recoil energy. The rate of the release of the incorporated atoms is determined by the state of the solid crystal lattice. This approach has been used to establish the correlation between the radioactive gas release and changes in the crystal structure for different samples of hematite [22]. Many reports published in the literature give a comparison of the results obtained with different versions of the emanation method [23–25]. It is of interest to note here the results obtained in an investigation of complex multi-stage processes in oxalate decomposition [23]. In the case of the classical version of the emanation method the radon atoms formed are located at a maximum depth of 300–400 Å and are generated continuously by the Ra decay. Radon atoms incorporated by the discharge are located at a depth of 10–30 Å from the surface. In the latter case the thermally activated inert-gas release due to diffusion and the state of the surface before incorporation of the radioactive gas label should be taken into account when interpreting the ETA results.

In most applications of the emanation method, a continuous measurement of inert gas release vs. time is needed. The ionization chambers for measuring the $\alpha$-activity used in many works [26,27] provide high efficiency and sensitivity ($10^{-11}$–$10^{-13}$ Ci). The details of the measuring techniques have been described previously [16]; scintillation detectors can also be used [28–30]. Geiger–Müller and semiconductor detectors can be used to measure the $\beta$ and $\gamma$ activity of radioactive inert gases [31].

Of particular interest is the use of the emanation method to study the changes that occur in solids (particularly catalysts); the study can be done directly, during the course of the reaction and during the preparation of the catalyst. Using emanation curves it is possible to follow the changes that occur due to ageing, dehydration, multi-stage changes in the crystal lattice of metal hydroxides, and changes in the surface, size of particles and the atom and ion mobility of the oxides produced. For many powders composed of crystals the temperature at which substantial displacement of atoms or ions in the lattice (Tamman temperature) starts and at which the rate of self-diffusion in ionic crystals increases has been determined by means of ETA. In oxides, for example, this temperature is approximately 0.5–0.6 of the melting point.

We have used ETA to study a number of reactions in solids taking place under higher temperatures, such as those used in the preparation of complex heterogeneous catalysts [32].

The specific-surface-area changes and $E$ at various temperatures and stages of dehydration of manganese, thorium and zirconium hydroxides has been reported [33]. Different behaviour was found for $^{85}$Kr at points of irreversible transition of $\beta$-quartz into $\beta$-crystoballite (270 °C) and $\alpha$-quartz into $\beta$-quartz (575 °C) was found, this being connected (according to the opinion of the author [34] with different types of phase transition [34]. The emanation method has also been used to establish the stages of thermal decomposition of manganese dioxide and the influence of the starting specific surface [35]. Gregory et al. [36] have described the results of an investigation of thoron diffusion during dehydration and the phase transition of alumina; good agreement between experimental and calculated values was noted. These authors found that $E$ is related to defects caused by the deviation from stoichiometry of the oxides. The influence on $E$ of the changes in defects and oxygen concentration has been described by Shibanova and Zhabrova [37]. The data obtained with the emanation method are in good agreement with the concept of defects in zinc and nickel oxides due to the formation of interstitial ions after doping by lithium and gallium ions.

The possibility of using emanation thermal analysis to observe solid phase transitions, the onset of decomposition, the increase in mobility of crystal lattice ions, and changes in dispersivity and defectiveness of solids has led to its application in investigating reactions in solids, in particular those used during the preparation of catalysts. The application of the emanation method in this field has been described by Schröder et al. [38]. It was found that the emanation method clearly establishes the presence of unstable states of zinc, beryllium and aluminium oxides under relatively low temperatures due to the Hedvall effect [39] which foresees an increase in the ion mobility and a relative maximum of both the physical and chemical activity in the transient state, in particular during the transformation of $\gamma$-alumina into $\alpha$-alumina.

The latter is of interest in investigations connected with chemisorption and catalytic processes on the surface of solids. During heterogeneous catalytic reactions many processes may take place on the surface of the catalyst which are clearly detected by the emanation method, e.g. changes in the catalytic surface, the formation of surface compounds, blocking of the surface by the reaction products and possible solid phase transitions.

It has been found [40] that about half of the radon incorporated by ion bombardment is released from the surface of the Pt catalyst when a hydrogen–oxygen mixture flows over it. Since the release of the gas label takes place mainly during the reaction of hydrogen with chemisorbed oxygen, the emanation method can be used to detect the location and distribution of active sites on the surface of the catalyst and to obtain, directly during the oxidation process, additional data concerning the reaction mechanism.

The emanating power of different oxide catalysts has been studied [7] both during the chemisorption of gases and vapours formed by the decomposition of isopropyl alcohol, and during the decomposition reaction itself. The results obtained show that physical adsorption does not practically influence on the emanating power of oxides, while the chemisorption of water, acetone and alcohol causes pronounced changes in the emanation of these oxides as well as in the rate of the decomposition reaction, especially in its initial stage.

Thus, since the 1950s and 1960s it has been shown that different modifications of the emanation method can be used successfully to solve different problems involving the state of the catalyst active surface in different stages of its preparation and use.

Systematic data on the application of gas-labelled surfaces to investigate catalysts and catalysis have been reported [16,25,41,42]. Several recent examples of this application are given below.

# INVESTIGATION OF THE DEHYDRATION OF HYDRATED ALUMINA (PREPARATION OF CATALYSTS)

Aluminium hydroxide is the starting substance for the synthesis of many catalysts. The thermal history of the aluminium hydroxide used determines the effectiveness and selectivity of the catalyst produced. Teplyakov [25] has investigated two such aluminium hydroxide samples, namely: hydrarghillite ($Al_2O_3 \cdot 4.6H_2O$) and böhmite $Al_2O_3 \cdot 1.9H_2O$). To incorporate the inert-gas atoms ($^{222}Rn$), the hydroxide samples were pumped down to $10^{-2}$ torr in a special vessel. The vessel was filled with radioactive gas ($^{222}Rn$) and a carrier (air) and a high-frequency electric discharge (15 kV) was applied to the external electrodes under a gas pressure of 0.05–0.5 torr. Under these

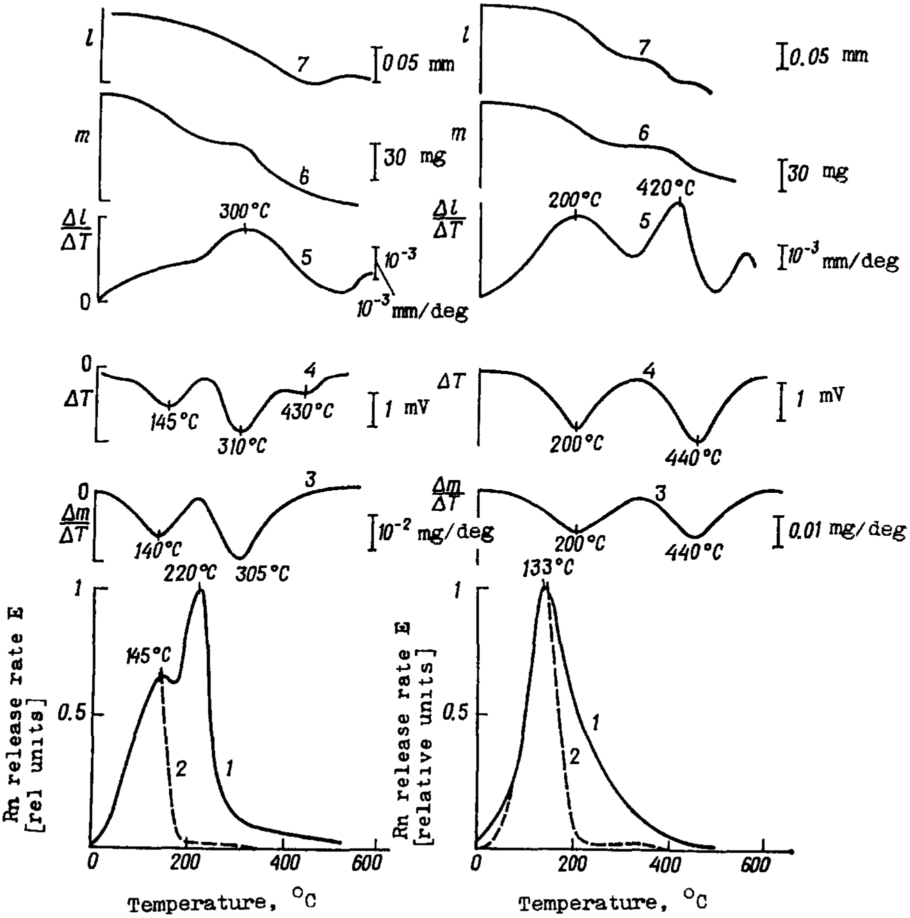

Fig 1 Results of thermal analysis of alumina hydroxide in air during linear heating. (left) hydrarghillite, (right) böhmite. Curves· (1) release of radon (ETA); (2) release of adsorbed water labelled with tritium (ETA); (3) differential thermogravimetry (DTG); (4) differential thermal analysis (DTA), (5) differential thermodilatometry; (6) thermogravimetry (TG); (7) thermodilatometry.

conditions the accelerated radon ions were embedded into the surface layer of the hydrarghillite or böhmite. The amount of radon released and tritium labelled water released was measured under conditions of linear heating using ETA and simultaneous TG/DTG DTA, and dilatometry (see Fig. 1). The radon release started at 60 ° C and two peaks were observed on the ETA curve at 145 and 220 ° C. Three endo effects were detected on the DTA curve (at 140, 310 and 430 ° C). The biggest weight losses took place in the temperature intervals 20–200, 225–350 and 360–500 ° C. The dilatometer detected sintering in the temperature intervals 20–170, 170–330, 330–450 and 450–700 ° C. The temperature intervals of the weight loss (TG) correspond to the maxima on the DTA curves (140 and 310 ° C).

The rate of release of the tritium labelled water reached a maximum at 140 ° C, confirming that all the tritium label was initially in the adsorbed state. The radon release curves reflect the processes of adsorbed water

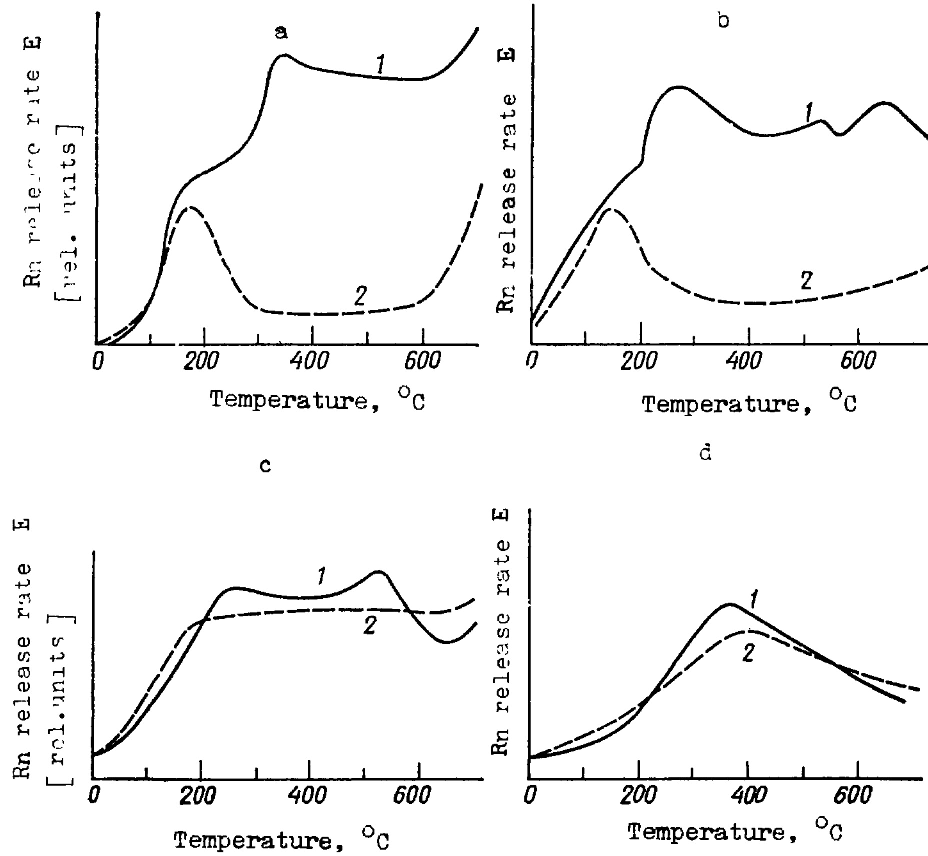

Fig 2. Temperature dependence of the rate of radon release ($E$) from oxide catalysts (linear heating, 7 ° C min$^{-1}$). (a) anatase $TiO_2$; (b) $\gamma$-$Al_2O_3$; (c) rutile $TiO_2$; (d) corundum $\alpha$-$Al_2O_3$. Curves: (1) heating in the absence of isopropanol flow; (2) heating in a flow of isopropanol.

evaluation (the first peak) and the dehydration of hydrarghillite itself (the second peak). In the latter case the radon release curve indicates the process of dehydration i.e. the inert radioactive probe indicates the existence of shrinking sphere kinetics for such solid phase processes. As shown in refs. 16 and 25, these processes are characterized by a spectrum of the activation energies. On the whole, the results obtained confirm the interglobular theory of aluminium hydroxide decomposition.

The ETA of böhmite enables us to reveal the onset temperatures of the formation of nuclei, the growth of crystals and the recrystallization of $\gamma$-$Al_2O_3$ [25].

## INVESTIGATION OF A HETEROGENEOUS CATALYTIC REACTION COURSE

The ETA method of an inert-gas radioactive probe was used to investigate the heterogeneous catalytic reaction of isopropanol decomposition over $TiO_2$ and $Al_2O_3$ catalysts. It should be noted that the dehydration takes place only over alumina, whilst dehydrogenation over titanium dioxide occurs at the beginning of the reaction followed by dehydration. The catalytic activity of oxides depends essentially on their crystal structure. For example, below 250 °C $\gamma$-$Al_2O_3$ and anatase are more active than $\alpha$-$Al_2O_3$ and the rutile form. This was shown by measuring the surface gas label (radon) released from the catalyst during heating in the presence of a flow of alcohol vapour: the increase in catalyst activity is accompanied by a sharp release (seen as a

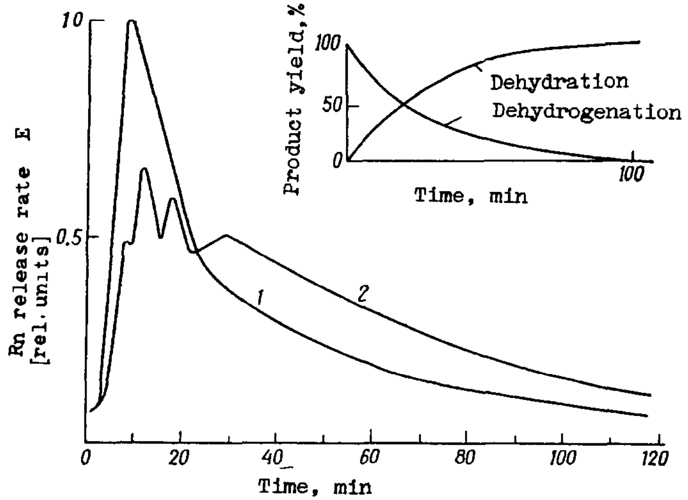

Fig 3 Isothermal (250 °C) release rate of radon during the catalytic decomposition of isopropanol in flow regime over $\gamma$-$Al_2O_3$ (1) and anatase $TiO_2$ (2). For comparison the relationship between the products of the dehydration and dehydrogenation reactions of iso-$C_3H_7OH$ over anatase are shown.

peak) of radon atoms originating from the subsurface layers of the solid (the depth of the radon atom incorporation is about 30 Å) (Fig. 2).

During isothermic experiments performed in a flow of isopropanol the release of radon was observed only for conditions under which catalytic reaction took place. The initiation of the reaction led to a sharp increase in the amount of radon released from γ-$Al_2O_3$ and anatase (Fig. 3) and to a

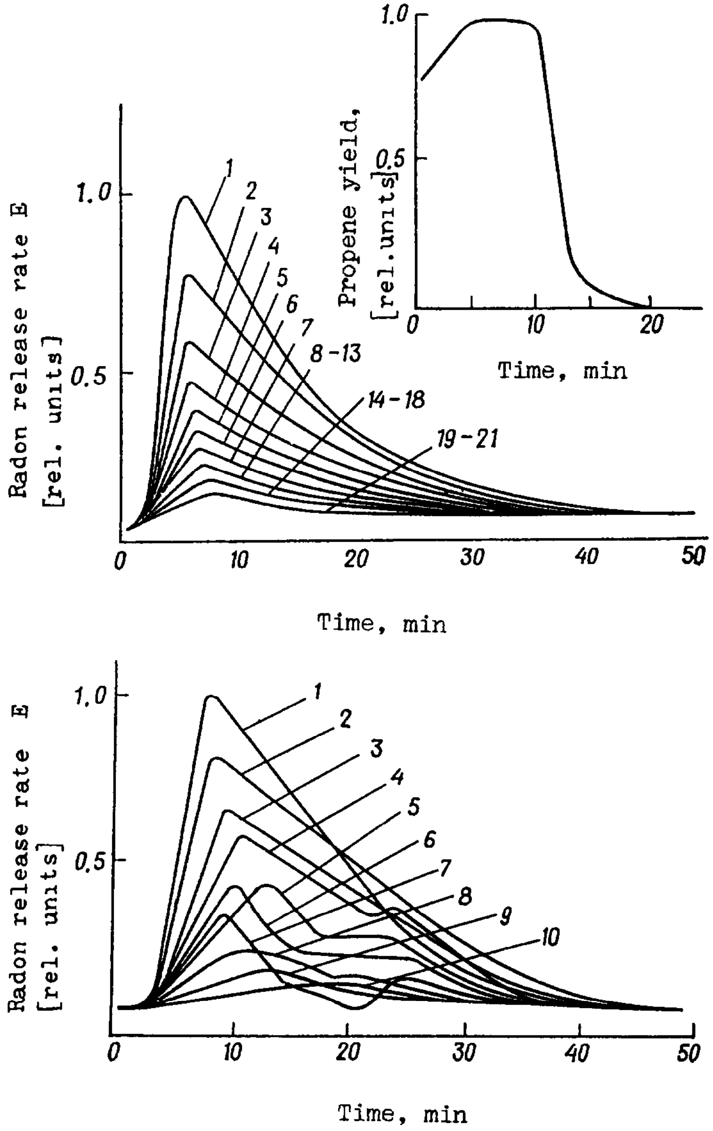

Fig 4 Release rate ($E$) of radon during isopropanol decomposition (pulse regime). (a) γ-$Al_2O_3$ ($T = 250\,^\circ C$); (b) anatase ($T = 280\,^\circ C$). The numbers on the curve indicate the number of pulses. The time dependence of propene yield after injection of an isopropanol sample (catalyst γ-$Al_2O_3$ anatase, $T = 250\,^\circ C$) is shown for comparison

negligible release of radon from orund and rutile. The radon release rate curve shows a peak with a long "tail". The radon release begins after 1 min, reaches a maximum after 5 min and continues for 120 min. The catalytic reaction over anatase is characterized by two peaks at 12 and 20 min and continues for 120 min. The data on the yield of the reaction products are shown in Fig. 3 for comparison.

Isothermal experiments using pulse injection of isopropanol showed that in the case of $\gamma$-$Al_2O_3$ (Fig. 4) after the injection of the isopropanol pulse over 5 s the radon release begins after 1 min, reaches a peak maximum at 5 min, and continues for 40 min. This was followed by gas chromatograph recording of the reaction products. The effect of the radon release was observed for a series of injections (up to 21), the position of peaks remaining constant with time while the heights of the peaks decreased. A similar chromatograph recording was obtained for anatase with the exception that the shift of the peaks over time took place over a series of injections, and after 4–5 injections the peak split into two peaks (change of the reaction mechanism). It is interesting to note that for used catalysts and the deposition of coke the regeneration of catalysts under elevated temperatures is accompanied by additional radon release. The above-mentioned data are evidence of the existence of a correlation between catalytic activity and the release rate of the inert gas label from the catalyst surface.

## CONCLUSION

The emanation method based on inert gas labelling of the surface is simple and universal. It can be used to detect solid phase transition features, including phase transitions without heat effects, and the temperature ranges of transitions, their kinetic parameters and the spectrum of activation energies to be determined. The method can be used to investigate heterogeneous catalytic reactions directly during catalysis and to obtain information about local interactions of the reagent with the catalytic surface and the site of catalytic action, and to observe the change in the types of catalytic site and the route of the reaction. Particularly valuable information can be obtained by combining this emanation method with other physico-chemical techniques, e.g. X-ray phase analysis, differential thermal analysis, dilatometric analysis and thermogravimetric analysis.

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