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Novel pulse thermal analysis method and its potential for investigating gas–solid reactions

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Abstract

The application of thermal analysis (TA) has been extended by developing a novel method, pulse thermal analysis (PTA). The method is based on the injection of a specific amount of the gaseous reactant(s) into an inert carrier gas stream and monitoring of the changes in the mass, enthalpy and gas composition resulting from an incremental extent of the gas–solid reaction. PTA enables carrying out gas–solid reactions with a controllable reaction progress at the desired temperature. It provides the opportunity of simultaneous monitoring of changes in the composition of the gas and solid phases during the course of the reaction. PTA can also be applied for quantitative calibration of mass spectrometric signals in combined TA–MS systems. The beneficial features of the new method for investigating reduction and oxidation of solids, heterogenous catalytic reactions, and for quantitative determination of the evolved species, are illustrated using various examples. © 1997 Elsevier Science B.V.

Keywords: Pulse thermal analysis; Thermal analysis coupled with mass spectrometry

1. Introduction

Due to the possibility of simultaneous monitoring of the mass changes and thermal effects caused by the chemical reactions or physical processes, e.g. crystallization or phase transformation, thermal analysis (TA) is widely applied for investigating gas–solid reactions. Some years ago, the potential of TA has been increased by its coupling with methods enabling the analysis of the evolved gaseous products such as mass spectrometry (MS) [1,2] or Fourier-transformed infrared spectroscopy (FTIR) [3].

Generally, TA is used for characterizing gas–solid reactions or decompositions of solids extending from zero to full conversion, i.e. the whole process is monitored. However, inspection of the total transformation and its application for calculating kinetic parameters are of little value, when data concerning a very small reaction extent are necessary. Important examples are catalytic reactions where initial rates of gas–solid reactions are required in order to investigate the possible changes in the solid phase during the reaction.

The modifications of the conventional TA proposed in the past two decades all ground on monitoring of the total course of the reaction, from zero to full conversion. New methods, such as controlled reaction rate TA (CRTA, Rouquerol [4,5]), quasi-isothermal and quasi-isobaric TA (Paulik et al. [6,7]), stepwise TA (Soerensen [8,9]), modulated (Reading et al. [10]), and alternating TA (Riesen et al. [11]) have increased

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the TA potential in specific applications providing, e.g. the possibility of decomposing solids with a constant rate (CRTA) or enabling the separation of the total heat flow into its reversing and non-reversing components (modulated and alternating TA). Events observed in the reversing heat flow are usually transitions which are thermodynamically reversible at the temperature at which they are detected (e.g. glass transitions and melting). Non-reversing events are usually non-reversible, e.g. cold crystallization of polymers and glasses or decomposition. As a result of the application of the last two methods, even a very small C_p change occurring during the cold crystallization can be detected.

In all mentioned modifications, the heating either follows a pre-determined temperature programme, or, as in CRTA or quasi-isothermal TA, the heating control involves a feed-back from the sample other than its temperature.

In the conventional TA, the experiments are carried out isothermally or with linear temperature change. Due to the experimental limitations, one cannot describe quantitatively the initial part of the reaction at a desired temperature. At the beginning of the experiment in the isothermal mode, the system has to reach the chosen, constant temperature. However, the reaction may already occur during the temperature settling. For the same reasons, it is impossible to quench the reaction at a desired time (or at a desired extent of reaction). Also in the Non-isothermal mode of changing the temperature in the system, the most popular operating of TA, One cannot decompose the sample up to a certain degree or quench the reaction at a certain time.

Another difficulty met in conventional TA, leading to an uncertainty in interpreting the results, is caused by the occurrence of simultaneous reactions, especially in multicomponent systems, when often two or more processes overlap. A typical example is the reduction of supported metal oxides, very often used as catalysts, where the weight loss due to the oxide reduction is overlapped by the continuous weight loss caused by dehydration of the support. This last process occurs generally in a wide temperature range, spanning from room temperature up to 1000°C. Another problem arises from the frequent low content of the reacting compound in multicomponent systems in conjunction with possible interferences of the monitored events. If, additionally, due to change in temperature or composition of the atmosphere, the buoyancy effect produces a shift in the TG curve in the range of a few hundred micrograms, it becomes rather unrealistic to interpret weight changes of this magnitude.

The novel pulse thermal analysis (PTA) method presented here has been invented to eliminate or at least reduce the aforementioned difficulties. According to the general rules of the International Confederation of Thermal Analysis, defining the various techniques of thermal analysis [12], PTA can be described as follows:

"Pulse thermal analysis is a group of techniques in which physical properties of a substance are measured as a function of temperature whilst the substance is subjected to a controlled-temperature programme and controlled changes in the composition of the reaction atmosphere performed in a pulse-mode. The measured properties of a substance are: mass, temperature difference between a substance and reference material and/or the difference in energy inputs into a substance and reference material, and the nature and/or amount of volatile products released by a substance."

The PTA method is based on the injection of a specific amount of the gaseous reactant into the inert carrier gas stream and the monitoring of the changes of the mass, enthalpy and gas composition resulting from the incremental reaction extent. The method is also suitable for the quantification of the evolved gas by MS or FTIR due to the injection of a well-known amount of the chosen gas to the system, which can be used for calibration. In contrast to conventional TA and all its modification, the control over the reaction is carried out not only by the temperature, but also by a change in the composition of the reactive atmosphere.

2. Experimental

Experiments were carried out isothermally or non-isothermally (generally applied heating rates were in the range of 5–10 K/min) on a Netzsch STA 409 thermoanalyzer equipped with a gas injector (dual-external sample injector, Valco Instruments) enabling injection of a certain amount of two different pure gases or gaseous mixtures into the system. The amount of injected gas could be changed from 0.01 to 10 ml.

Mainly 0.25, 0.5 and 1.0 ml volumes were used. Gases evolved during reaction and/or injected into the system were monitored on-line with a Balzers QMG 420 quadrupole mass spectrometer, connected to the thermoanalyzer by a heated (ca. 200°C) capillary.

3. Results

In the following, a series of examples will be presented which illustrate the characteristic features of PTA. Although these examples originate from the use of PTA in catalytic research, similar applications are conceivable in all other areas where thermal analysis has proven to be a potent tool.

3.1. Gas–solid reactions with desired extent of reaction at a specified temperature

When interpreting the results of gas–solid reactions studied by conventional thermal analysis, difficulties can arise by experimental limitations. The investigation of the course of the reaction is rather difficult under isothermal conditions at temperatures at which the reaction proceeds with high rate. Before the constant temperature is reached, after introducing the sample to the system, considerable progress of the reaction can take place under not-well-defined conditions. In such a situation, the data describing the beginning of the reaction are of little value.

In contrast, using PTA, the desired temperature is reached under inert atmosphere and the injection of the reactive gas takes place at a well-defined temperature. An example illustrating this characteristic is given in Fig. 1 which describes the isothermal reduction of copper oxide by hydrogen at 450°C. Each pulse (1.0 ml of hydrogen) extended the reduction progress by ca. 0.035. After 10 pulses, presented in the upper part of Fig. 1, the total reduction progress reached 0.332, corresponding to one-third of oxygen having been removed from the cupric oxide. The mass spectrometric signals of $m/z = 18$ clearly indicates that desorption of water produced during CuO reduction is slow, which is in agreement with the common opinion concerning the kinetics of this process stating that water desorption is the rate-limiting step [13].

A very important feature of PTA is that the reaction stops between pulses, providing the opportunity for producing solid samples with well-defined composition. The CuO sample (50.02 mg) lost 0.353 mg of oxygen after the first pulse of hydrogen, i.e. 3.53% of the weight loss expected upon total reduction. Stopping the reduction after the required number of pulses and/or changing the pulse volume makes it possible to obtain samples with any required reaction extent, what enables to investigate the changes in the product composition as a function of the reaction progress.

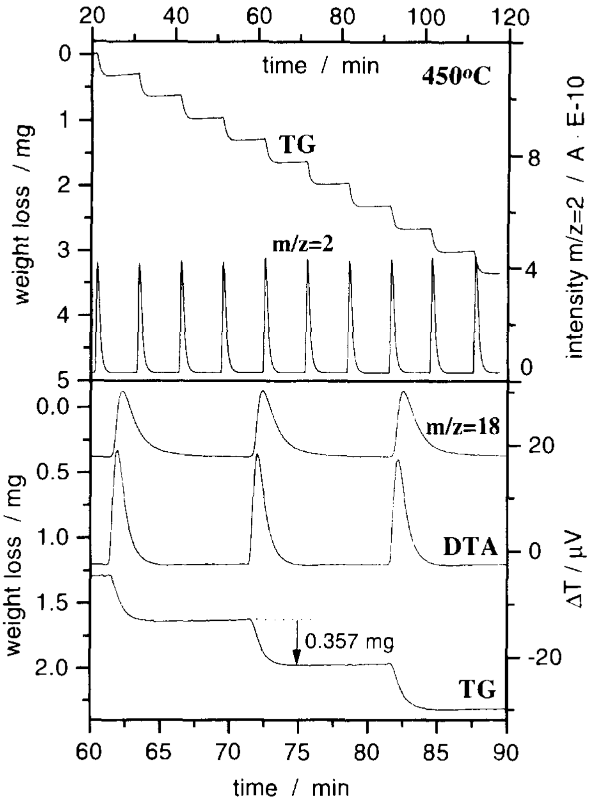

Fig. 1. The reduction of CuO by the hydrogen pulses at 450°C.

This procedure was applied for the investigation of the composition of the CuO reduction product. There is a controversy in the literature concerning the course of this reduction: generally, it is assumed that CuO is reduced by hydrogen to metallic copper without intermediates [14,15]. On the other hand, there are suggestions that Cu_2O is formed in the first stage of the reduction [16,17]. The samples produced by means of PTA, corresponding to a different total reduction extent, were analyzed by X-ray diffraction (XRD): the results of these investigations are presented in Fig. 2. The upper part of the figure shows the XRD

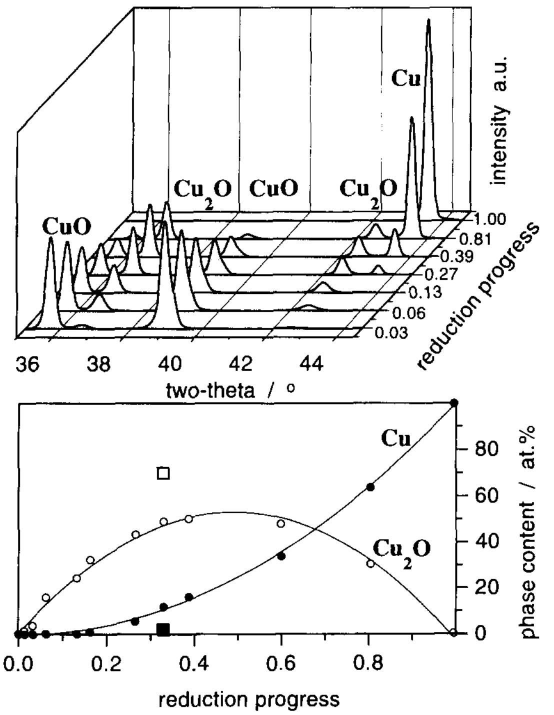

Fig. 2. The XRD patterns of the products of CuO reduction at 450°C (top) and the phase composition of the products (bottom) as a function of the reduction extent.

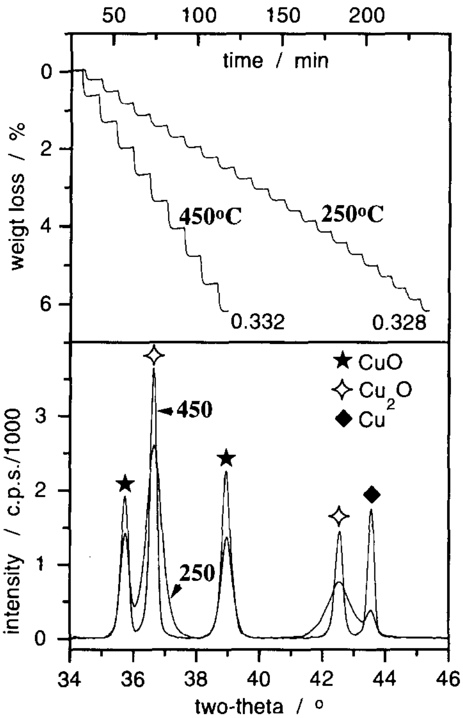

Fig. 3. The comparison of the TG curves (top) and XRD patterns (bottom) obtained by means of PTA at 450 and 250°C, respectively.

patterns of the products of the CuO reduction as a function of the reduction extent (changing from 0 for CuO to 1.0 for Cu). Clearly visible is the formation of the diffraction-pattern characteristic of Cu_2O. The lower part of Fig. 2 depicts the results of the determination of the phase composition calculated from the intensities of the most intensive reflections (111) of the respective compounds. Cu_2O is present in the full range of the CuO reduction.

In order to compare the course of the reaction at different temperatures, CuO was reduced by means of PTA at 250°C by 1 ml pulses of hydrogen (Fig. 3). Due to the much lower rate of the reduction at this temperature, each pulse resulted in ca. 1.5% change in the reaction extent only and a reduction progress comparable to those obtained in the experiment performed at 450°C (0.332) was reached after 22 injections (see Fig. 3, upper part). The results of the XRD analysis of both reduction products with almost identical extent of reduction are presented in the lower part of Fig. 3. The amount of the respective products of CuO reduction at 250°C is marked by squares in the lower part in Fig. 2.

Due to the possibility of carrying out the reaction at a required temperature, PTA allows the separation of the reactions occurring simultaneously. The comparison of the determination of the Cu content in alumina-supported catalyst by the reduction of CuO with hydrogen by means of conventional TA and PTA is presented in Fig. 4. The reduction of CuO investigated by conventional TA is shown in the upper part of the figure. TG, DTA, and $m/z = 18$ curves indicate that two processes occur simultaneously. Dehydration of aluminium hydroxide begins at room temperature as emerges from the continuous weight loss starting at 30°C accompanied by the weak endothermal effect observed on DTA and a broad peak on the $m/z = 18$ curve. Starting from ~ 150°C, the dehydration of the support is overlapped by the exothermal reduction of CuO (note the exothermal effect in DTA together with the weight loss and evolution of water). The weight loss due to CuO reduction calculated from the con-

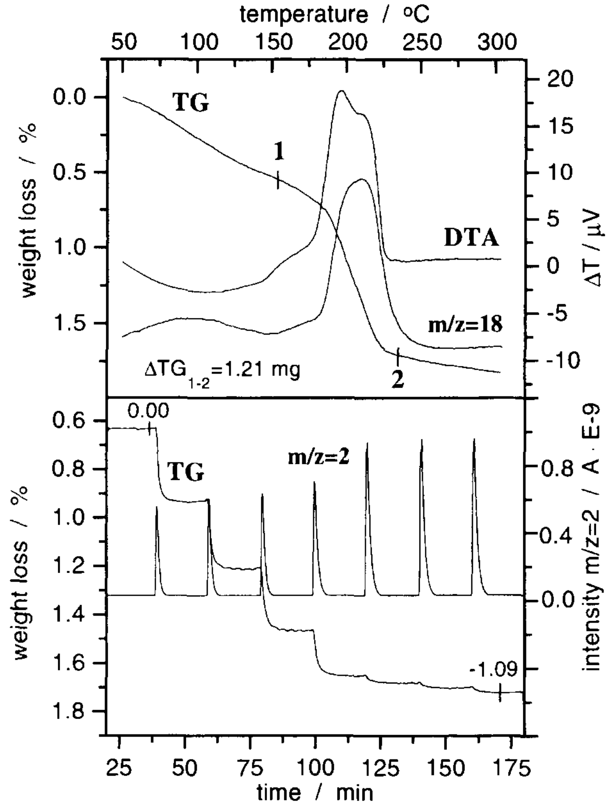

Fig. 4. The reduction by hydrogen of the alumina-supported CuO carried out by means of the conventional TA (top) and PTA (bottom). Sample weight 20.10 mg.

ventional TG curve is ca. 10% greater than those obtained by PTA, because calculation of the exact weight loss only due to the reduction is uncertain, what leads to an imprecise determination of the amount of CuO.

Using the PTA method, the sample was dehydrated at 350°C till the weight loss caused by the water evolution was negligible, and reduced progressively by 1 ml pulses of hydrogen. TG curve and $m/z = 2$ signal are depicted in the lower part in Fig. 4. The observed weight loss is caused by the reduction only and the determination of Cu content is much more accurate.

When quantifying the TG signals in conventional TA, one has to take into account the apparent change in the mass arising from the buoyancy effect. The influence of the buoyancy effect on the course of the TG curve, due to the change in the density of the gaseous atmosphere in the thermoanalytical chamber, is caused by the increase in the temperature during the experiment. This phenomenon is additionally complicated in the case of rapid exothermal reactions and changes in the composition of the atmosphere. All these problems render the interpretation of the thermogravimetric results questionable when the weight loss resulting from the investigated reaction is of the magnitude as the apparent change in the mass produced by the buoyancy effect (e.g. during analysis of multicomponent systems when the amount of decomposed phase is in the range of only few percent). Also, when the reaction occurs during changing of the atmosphere in the oven, the exact quantification of the mass changes is difficult. The buoyancy effect caused by the change in the atmosphere in the thermoanalyzer chamber is demonstrated in Fig. 5. The results presented were obtained at a constant temperature (30°C) with two empty platinum crucibles (volume, 0.085 ml) and a Netzsch DSC-sample holder. The change in the atmosphere from hydrogen to nitrogen leads to the apparent weight loss of 0.462 mg due to the large difference in the density of the gases. Even such a small difference in the densities as that caused by replacing nitrogen by oxygen produced the observable shift in the TG base line.

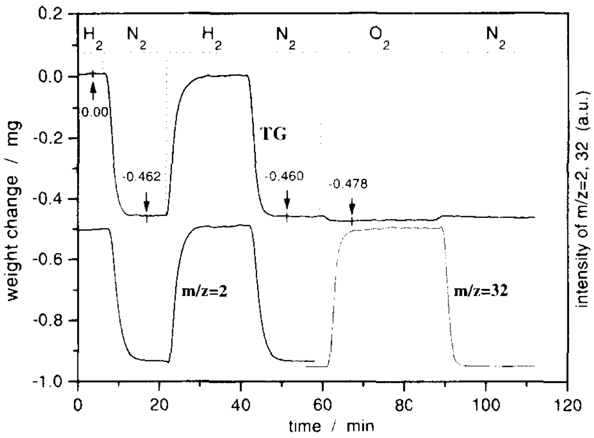

Fig. 5. The buoyancy effect resulting from the change in the atmosphere in the TA chamber. The apparent mass changes marked on the curves are expressed in milligrams.

The observed phenomena depend on the experimental settings (e.g. the volume of crucibles, the geometry and size of the sample holder, the volume of the sample and reference material), but even for the

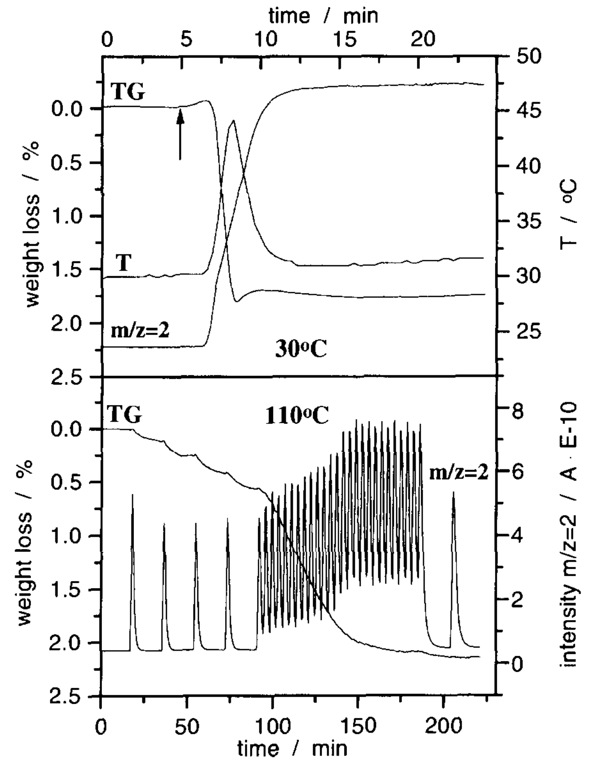

Fig. 6. The reduction of the zirconia-supported PdO by hydrogen investigated by means of the conventional TA (top) and PTA (bottom). The arrow indicates the moment of the change of the atmosphere from pure argon to 20 vol% of hydrogen.

experiments performed under suitable conditions, one cannot eliminate the influence of the buoyancy on the thermogravimetric curve. In the case of reactions occurring at temperatures at which the atmosphere in the chamber is changed, the conventional thermal analysis gives results with some degree of inaccuracy. This scenario is illustrated using the reduction of PdO supported on zirconia by hydrogen carried out by means of conventional TA, shown in the upper part of Fig. 6. The reaction was investigated at 30°C: after five minutes, the atmosphere in the system was changed from argon to hydrogen. The moment of admission of hydrogen into the chamber is marked on the TG curve by an arrow. The reduction of PdO already started during the period of the changing of the hydrogen concentration (note the initial weight gain caused by the change in the atmosphere, followed by the weight loss due to reduction). Not only the beginning, but also the end of the reaction was still disturbed by the buoyancy effect and the reduction was almost complete before the concentration of hydrogen reached a constant value, indicated by the course of $m/z = 2$ signal showing the concentration of the hydrogen in the system. The reduction of the supported PdO occurred under not well-defined conditions. During the reaction, the concentration of hydrogen was changed from 0 to 25 vol%, and the temperature increased from 30 to 44°C at the point of the maximal reduction rate due to the large exothermal effect of the reduction. Both effects, i.e. the change in the density of the gaseous atmosphere and the rapid change in the temperature, led to the large shift in the TG curve, making its interpretation very difficult. The TG curve presented in the upper part of Fig. 6 does not allow stoichiometric calculations of the investigated process. The observed course of the TG signal is the sum of superimposed processes, influencing its shape, and an exact determination of the beginning and the end of the reduction cannot be made.

In order to avoid these difficulties, the second experiment with the same mass of the reactant (100.0 mg, PdO loading 24.9 wt%) was carried out with PTA. The first four pulses (1 ml of hydrogen) were injected at 110°C, each 20 min, in order to observe the first period of the reduction. The weight loss of the supported PdO caused by the injections of hydrogen (presented by the mass spectrometric signal $m/z = 2$) is depicted in the lower part of Fig. 6. As emerges from this figure, the beginning and the end of the investigated process is clearly visible and the calculation of the weight loss due to the reduction is much more accurate compared to the results gained with conventional thermal analysis.

3.2. *Measuring of the initial rate of gas–solid reactions*

Very often, during investigations of the gas–solid reaction, the knowledge of its rate at the beginning of the process is very important. If the catalytic reaction occurring on the surface of a supported catalyst proceeds via a reduction and re-oxidation cycle of the catalytically active phase, its investigation by conventional thermal analysis is biased by at least two reasons: (i) due to low loading of the active phase on the support, the observed changes caused by the reduction may have the same magnitude as the

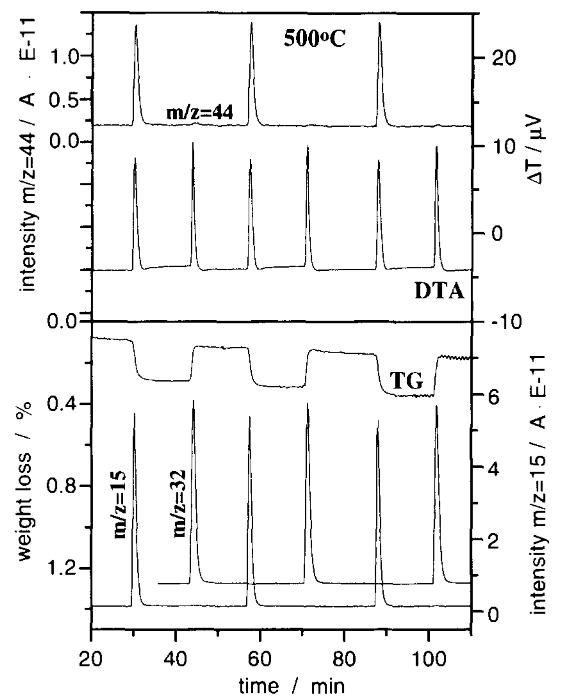

Fig. 7. The reduction of the zirconia-supported PdO by the pulses of methane and its subsequent re-oxidation by the oxygen pulses. During each pulse, the change in reaction extent is in the range of 0.05.

changes caused by the evolution of water from the high-surface-area support, rendering the interpretation difficult and (ii) the investigation of the reduction or oxidation processes in conventional experiments is generally performed for the total extent of the reactions, and, consequently, it is very difficult to gain proper information on the beginning of the process, where the reaction extent is only a few percent. Additionally, the prediction of the reaction course based on kinetic parameters calculated from the total extent of the reaction is sometimes of little value when the very small reaction extent has to be considered.

The application of PTA provides the opportunity of measuring the rate of any gas–solid reaction at its beginning. Depending on the temperature and the volume of the injected reactive gas, the reaction can be investigated in the range of reaction extending smaller than 1%.

Results presented in Fig. 7 describe the reduction of the supported PdO by methane followed by the re-oxidation of the metallic Pd by oxygen at 500°C. The pulse volumes applied were 0.25 ml for methane and 1.0 ml for oxygen. The aim of these investigations was to check the possible occurrence of a so-called Mars–van Krevelen (MVK) mechanism during the catalytic combustion of CH_4 over Pd-containing catalysts. The detailed results of the mechanism investigations are reported in [18]. As emerges from TA and MS signals depicted in Fig. 7, the weight changes due to reduction and oxidation during pulses of CH_4 and O_2, respectively, are almost equal. The observed fact that the rate of the reduction and re-oxidation are similar is a necessary pre-requisite for the simultaneous occurrence of the redox sequence, and thus the existence of a MVK mechanism. The results of similar experiments performed at 300°C (not shown) indicated that at this temperature, the rate of the PdO reduction during the first pulses was higher than the rate of the Pd re-oxidation.

3.3. Simultaneous monitoring of the changes in mass, enthalpy and gas composition

The main characteristic of PTA is that the reaction occurs only during a relatively short period of time due to the injection of a small amount of the reactive gas into the inert carrier gas stream. The possibility of monitoring simultaneous changes in the mass (not disturbed by the buoyancy effects), thermal effects and the composition of gaseous reactants and products renders PTA a versatile tool for investigating gas–solid reactions. This will be illustrated next using, as an example, the investigation of the catalytic reaction between methane and oxygen over Pd-containing catalysts. PTA, in conjunction with simultaneous measuring of the variation in the composition of gas and solid phases during the course of reaction and application of a labelled catalyst, provided answers to the following questions concerning the evaluation of the mechanism of the catalytic reaction [18].

(i) Is the total reduction and/or the total oxidation of the catalytically active phase possible under the reaction conditions applied?

(ii) Which phase, Pd or PdO, is dominant under stationary reaction conditions?

(iii) Does a redox mechanism, involving lattice oxygen, contribute to methane combustion?

(i) In order to investigate possible compositional changes in the solid catalyst during the catalytic reaction of methane, it was necessary to study the course of the redox reactions in the system Pd–PdO–CH_4–O_2 at the pertinent temperature. During the previously described experiments, depicted in Fig. 7, the composition of the catalyst changed only slightly after each pulse (the reaction extent was in the 0.04–0.05 range). Moreover, after two pulses, the catalyst reached its starting composition because the rates of reduction and oxidation were equal. The aim of the experiments presented below was to check whether both reactions, i.e. the reduction of PdO and oxidation of metallic Pd, can be completed under the conditions applied (temperature, concentration of gaseous reactants and duration of pulse). The results of the reduction of supported PdO/ZrO_2 by methane and re-oxidation of the formed metallic Pd by oxygen after total reduction of PdO are presented in Fig. 8. The reduction of the PdO by 1 ml pulses of methane is clearly visible on the TG curve in the form of four distinct steps and corresponding exothermic effects on the DTA curve. The mass spectrometric signal of $m/z = 2$ indicates that metallic Pd, formed already after the first pulse of methane, catalyzes the decomposition of CH_4 and results in hydrogen formation. After the total reduction of PdO (during the fifth pulse), the DTA curve shows only the endothermic effect of the methane decomposition. The TG curve indicates the small weight gain after each methane pulse caused by the deposition of carbon produced during methane decomposition. Note also the formation of hydrogen in this reaction ($m/z = 2$).

Metallic Pd formed after the total reduction was subsequently oxidized by 1 ml pulses of oxygen. XRD analysis of the reaction product after five oxygen pulses confirmed the formation of PdO.

The results clearly indicate that in the investigated system, due to the presence of reductive (methane) and oxidative (oxygen) agents, both metallic Pd and PdO can exist, depending on the composition of the atmosphere and temperature. At higher temperatures, PdO decomposes (the partial pressure of oxygen over bulk PdO is equal to the partial pressure of oxygen in the gaseous mixture containing 4 vol% of O_2 at 736°C [19,20]). Generally, it is accepted that PdO is an active phase under reaction conditions in lean mixtures of methane and oxygen [21–23], but, even recently [24], it has been stated that Pd is more active for methane oxidation than PdO.

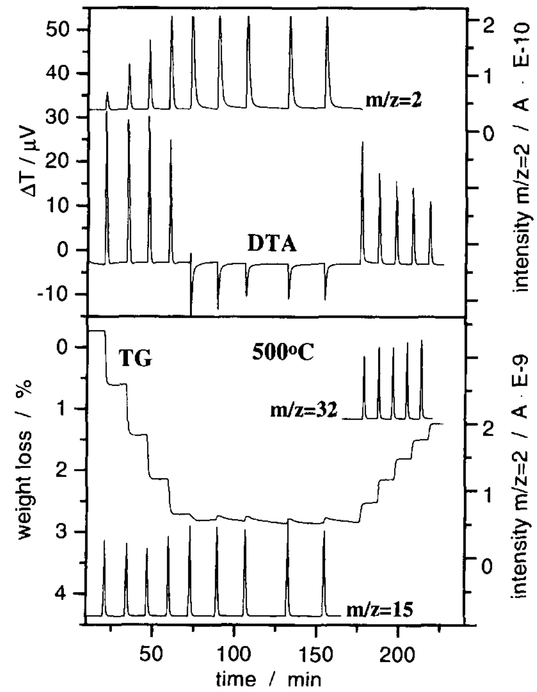

Fig. 8. The total reduction of the zirconia-supported PdO by the pulses of the methane followed by the oxidation of the metallic Pd by the oxygen pulses. Note the methane decomposition leading to the hydrogen formation.

(ii) The application of PTA could resolve the question concerning the composition of the active phase in Pd-containing catalysts due to monitoring of the thermal effects, changes in the catalyst mass and the composition of the gaseous products. The course of the catalytic reaction carried out with the reduced form of the catalyst, i.e. Pd/ZrO_2, is presented in Fig. 9. 1 ml pulses of the mixture $CH_4 : O_2$ with the volume ratio 1 : 4 were injected at 500°C. The thermogravimetric curve clearly indicates the weight gain after each pulse, together with the exothermic effect of the methane combustion. An exo-peak is followed by the broad, weak endothermic desorption of the water produced together with CO_2 during the combustion. After three pulses (point B marked by an arrow on TG curve), the catalyst was quenched and analyzed by XRD: the results of the XRD analysis are depicted in Fig. 10. XRD patterns indicate that the sample A (before catalytic reaction) contains Pd supported on monoclinic and tetragonal zirconia. After three pulses of the mixture of methane and oxygen, the amount of

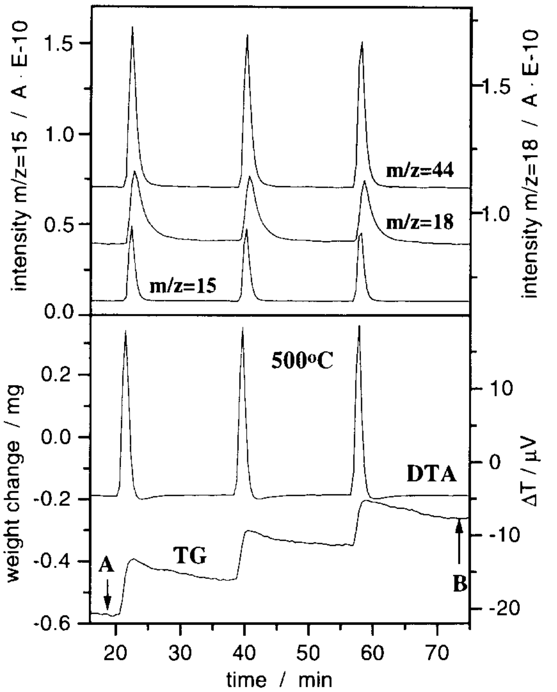

Fig. 9. TA and MS signals resulting from the pulses of the $CH_4 : O_2$ mixture over Pd/ZrO_2 catalyst. The XRD analysis of the solid phase was carried out at the points marked as A and B.

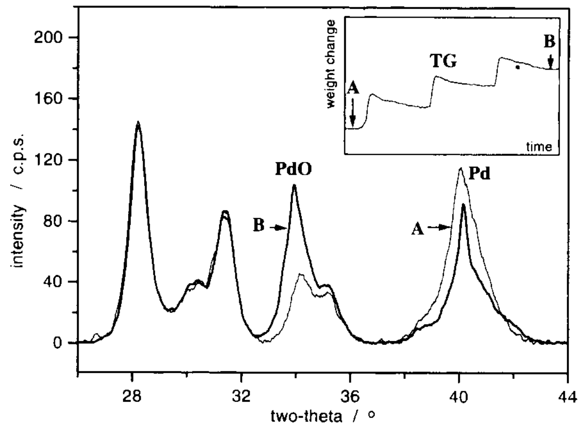

Fig. 10. XRD patterns of the Pd/ZrO_2 catalyst after three pulses of $CH_4 : O_2$ mixture at 500°C.

Pd in the catalyst decreases with simultaneous formation of PdO (see patterns of sample B). The results presented in Figs. 9 and 10 confirm that at 500°C, the stable, catalytically active phase is PdO.

(iii) PTA was applied for investigating the mechanism of the catalytic methane combustion. There is debate in the literature whether this reaction occurs as a normal surface reaction of the Langmuir–Hinshelwood or Eley–Rideal type or includes lattice oxygen of the catalyst (so-called Mars–van Krevelen or redox mechanism). Both possible mechanisms are schematically depicted in Fig. 11 for a catalyst containing $Pd^{18}O$. Although the redox-type mechanism is widely accepted, its experimental verification is difficult and mostly based on the comparison of the rates of the redox processes (oxidation and reduction) at the reaction temperature. The application of a labelled catalyst containing $Pd^{18}O$ together with PTA provided interesting possibilities for investigating the mechanism of this reaction. According to the scheme in Fig. 11, both considered mechanisms will lead to a different composition of the gaseous products. In the case of a pure surface reaction between adsorbed species, gaseous products, i.e. water and carbon dioxide, will not contain ^{18}O formerly present in the solid catalyst. If, however, the reaction between methane and oxygen proceeds according to the redox mechanism, involving the reduction of PdO with methane and subsequent reoxidation of Pd by oxygen, than the gaseous products should contain ^{18}O originating from the solid catalyst.

In order to discriminate between these mechanisms, pulses of the reaction mixture, containing CH_4 and O_2 in the 1 : 4 ratio, were admitted to the $Pd^{18}O/ZrO_2$ catalyst at 500°C. The preparation of the catalyst and the experimental details are described in [18]. TA and MS curves illustrating the catalytic combustion of methane are shown in Fig. 12. As emerges from the TG curve, PdO was not reduced under experimental conditions. A small, continuous weight loss resulted from evolution of water from the high-surface-area support. After each pulse of reactant mixture, TG indicates a distinct weight gain caused by the adsorption of the reactants and products, followed by their slow desorption. The endothermic process of the product desorption is also clearly visible on the DTA curve. Note the broad, endo-peak following the exothermic peak caused by the methane oxidation. Mass spectrometric signals indicate the formation of the gaseous products containing ^{18}O ($H_2{}^{18}O$, $m/z = 20$; $C^{18}O^{16}O$, $m/z = 46$; and $C^{18}O_2$, $m/z = 48$; not shown) confirming the role of lattice oxygen in the catalytic reaction.

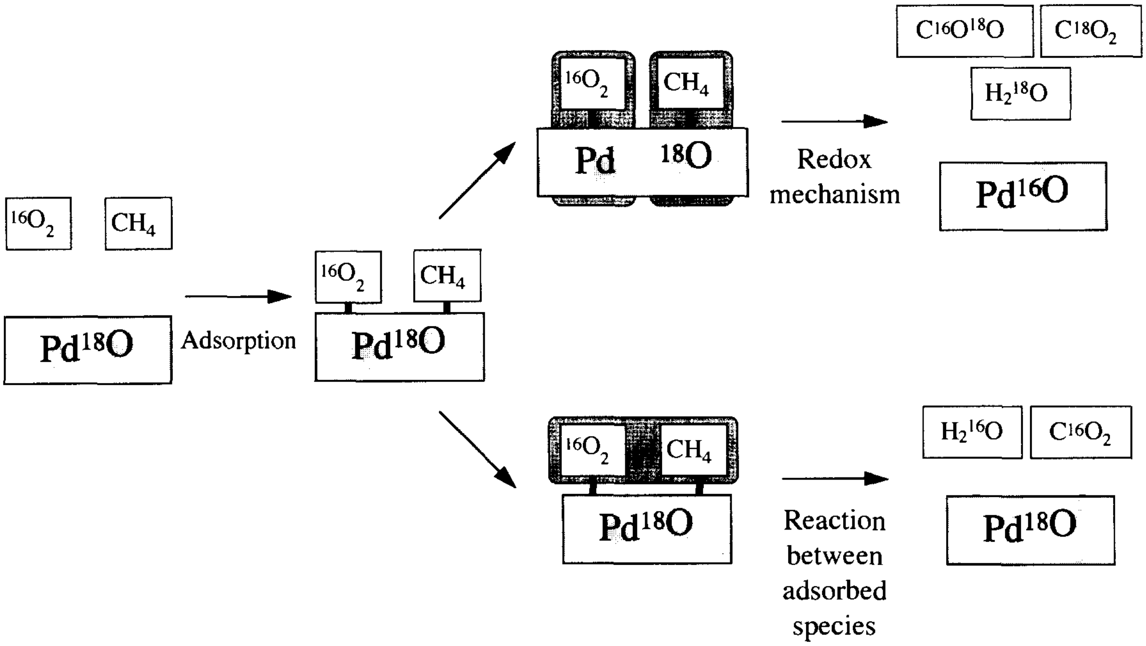

Fig. 11. The scheme of two possible mechanisms of methane combustion over $Pd^{18}O$. Note that products containing ^{18}O atoms are formed only when the oxygen from the catalyst lattice takes part in the reaction.

3.4. Quantification of mass spectrometric signals measured in combined TA–MS systems

Another interesting feature of PTA is that it allows a direct calibration of the mass spectrometric signals. The calibration is carried out by introducing into the TA–MS system a known amount of the investigated gas and determining the relationship between the amount of the gas and the intensity of the MS signal. A specified amount of the gas can be introduced to the system either by the decomposition of suitable solids via well known, stoichiometric reactions or by injection of a known volume of the gas into the carrier gas stream flowing with a constant rate. Detailed descriptions of both methods have been reported in [25].

The intensity and shape of the MS signal, recorded in the system in which a thermoanalyzer and a mass spectrometer are coupled by a capillary, depends on many factors. The construction of the pressure-reduction system, the kind of flow of the gas mixture into the vacuum chamber of the mass spectrometer (molecular or viscous), the pressure in the mass spectrometer, the temperature of the analyzed gas, influencing its density and viscosity, and the ratio of the flow of the analyzed gas to the flow of the carrier gas are only some of the experimental parameters changing the quantitative characteristic of the MS signal. Its theoretical calculation is rather complicated due to the lack of precise parameters, such as the exact temperature and composition of the gas entering the mass spectrometer. Both these values continuously change during the experiment. From a practical point of view, most of these difficulties can be avoided by calibrating the system at conditions similar to those during the measurement.

In order to check the influence of the temperature on the shape and intensity of the MS signal, pulses of oxygen and carbon dioxide were injected into the stream of carrier gas (argon) at room temperature and at 600°C. The results shown in Fig. 13 indicate that despite the change in the signal shape caused by the different temperature dependence of the convectional and diffusional flow properties of the carrier gas, the intensity of the mass spectrometric signal is almost constant in the range of 600°C. The numbers on the curves $m/z = 32$ and $m/z = 44$ indicate the integral intensities of the respective signals in arbitrary units.

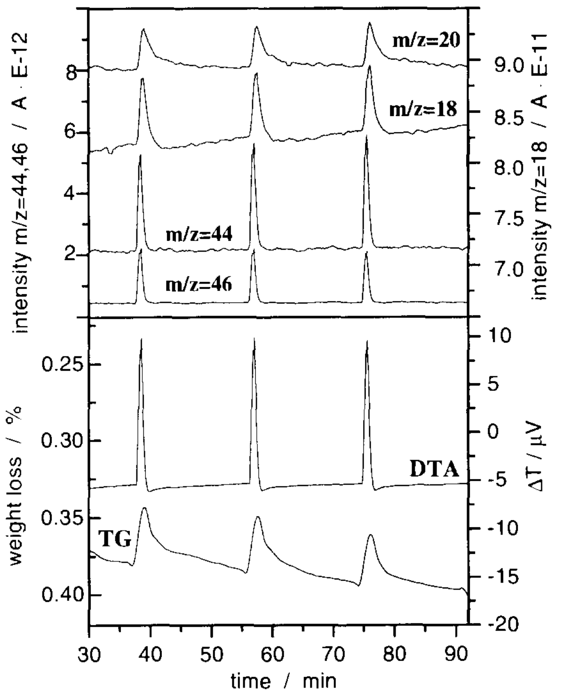

Fig. 12. TA and MS signals resulting from the reaction between CH_4 and O_2 over PdO/ZrO_2 carried out by means of PTA. Note the formation of the product species containing ^{18}O ($m/z = 20$ and 46 for $H_2{}^{18}O$ and $C^{18}O^{16}O$, respectively).

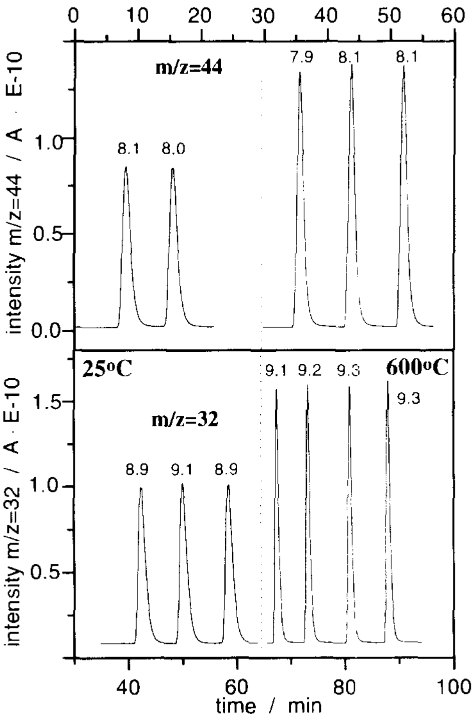

Fig. 13. Temperature dependence of the shape and the intensity of the MS signals for CO_2 ($m/z = 44$) and O_2 ($m/z = 32$). The numbers on the respective signals representing the integral intensities are expressed in an arbitrary unit.

Fig. 14 illustrates the use of PTA for the quantification of the evolved gases during TA–MS measurement of a zirconia aerogel in air. The sample was prepared by an acid-catalyzed alkoxide-sol-gel route with tetrabutoxyzirconium(IV) and subsequent high-temperature supercritical drying at 300°C [26]. The observed weight loss is caused by the evolution of physisorbed water and oxidation of organic residues present in the aerogel. The formation of CO_2, indicated by the exothermic effect on the DTA curve and the accompanying signal of $m/z = 44$ centred at 357°C, indicates the presence of organic residues in the aerogel matrix. In order to calibrate quantitatively the $m/z = 44$ signal, a 1 ml pulse of CO_2 was injected at the end of the experiment at 550°C (injected CO_2 is marked in Fig. 14 by the grey rectangle). The comparison of the integral intensities of the CO_2 signals, produced by the combustion of the organic residue during heating in air with the known amount of injected gas, provides the possibility for the determination of the carbon content of the investigated material. The amount found from the quantification of the MS signal (1.9 wt%) was confirmed by elemental analysis (2.0 wt%).

The investigated sample was X-ray amorphous, its crystallization is represented by the sharp exothermic peak centred at 492°C. During crystallization, the rest of the residual species trapped in the amorphous network is evolved. Note the evolution of water ($m/z = 18$) and small peak of CO_2 (its magnification, marked as 'A' is presented in the inset placed in the left upper part of the figure). The amount of the carbon released during the zirconia aerogel crystallization determined from the MS signal is equal to 0.007 wt%.

4. Discussion

The pulse thermal analysis extends the versatility of the conventional thermoanalytical methods by provid-

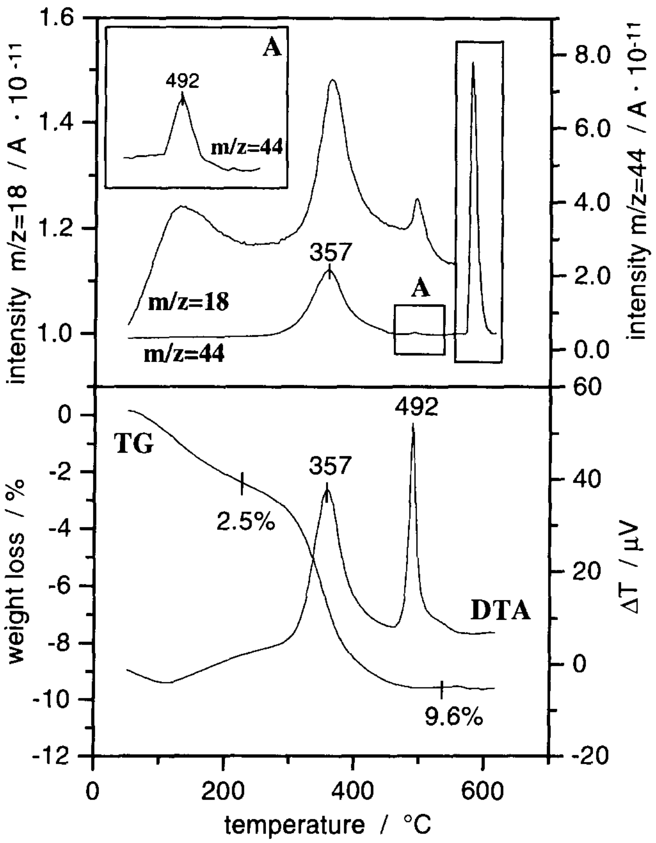

Fig. 14. TA and MS signals resulting during the calcination of the ZrO_2 aerogel in the air. The grey rectangle indicates the $m/z = 44$ signal formed by the injection of 1 ml of CO_2. The inset A presents the evolution of CO_2 occurring during the aerogel crystallization.

ing a means of the study of small reaction progresses which combines this advantage with all the possibilities of thermogravimetry, differential thermal analysis or differential scanning calorimetry and evolved gas analysis. Specifically, PTA offers the favourable features described in the following subsections.

4.1. The reaction can be stopped almost at any required reaction extent

Gas–solid reactions when investigated by PTA occur only during the duration of the pulse, what permits the investigation of the reaction product(s) corresponding to a well-known reaction progress. This provides the possibility of an exact determination of the solid-phase composition. This feature of PTA has been illustrated by the results concerning the reduction of CuO by hydrogen. The formation of the intermediate product Cu_2O proceeds continuously together with the formation of metallic copper. Due to the simultaneous occurrence of both processes, the thermoanalytical curves (TG, DTG and DTA) do not indicate the formation of the intermediate and only one step is visible on all TA signals. In some earlier reports concerning the reduction behaviour of CuO, the existence of the stages observed during the reduction of the supported CuO has not been explained by the formation of the intermediates, but as a consequence of a strong metal–support interaction [13,27]. The results obtained by means of PTA confirmed the presence of Cu_2O in the reduction products.

4.2. The reaction can be performed at any temperature

Applying PTA one can avoid the difficulties with the interpretation of the initial reaction period caused by the unstable conditions at the beginning of the

Table 1
Apparent weight gains in micrograms due resulting from a change of the atmosphere from the carrier gas to the gas mixture containing hydrogen assuming a total volume of the sample holder, crucibles, sample and reference material of 1 ml

	H_2 concentration (vol %)					
Carrier gas	1	5	10	20	50	100
Ar	16.9	84.5	169.0	338.0	844.8	1689.7
N_2	11.6	58.1	116.2	232.4	581.1	1162.2
He	0.9	4.5	8.9	17.8	44.6	89.2

experiment. Isothermal experiments cannot be done at temperatures where the reaction proceeds with a high rate, because of the uncontrolled reactions which may occur till temperature equilibration is attained. The reduction of supported PdO by methane and the reoxidation of metallic Pd cannot be investigated by conventional TA at 500°C due to very high reaction rates at this temperature.

In the case of two or more simultaneous reactions, e.g decomposition and gas–solid reaction, the application of PTA can help in separating the superimposed processes. As emerges from the comparison of the results gained by conventional TA and PTA, in the case of the reduction of supported CuO (Fig. 4), PTA enables a more exact determination of the weight loss due to reduction when this is interfered by weight loss due to support dehydration.

An interesting feature of PTA is the possibility of investigating the course of reactions occurring at room temperature such as reduction of metal oxides or oxidation of metals. When the gas–solid reaction starts at room temperature, its investigation by conventional TA will need the application of a cooling device. The exchange of the atmosphere in the system from inert to the reactive atmosphere has to be done at a temperature lying below the beginning of the reaction. The results of the reduction of supported PdO shown in Fig. 6 indicate that the reaction had already occurred to a significant extent under an unstable hydrogen concentration. In a recent paper [28] concerning the interaction of oxygen with alumina-supported Pd, the oxidation of Pd at room temperature was shown to occur during introduction of oxygen into the system. Two difficulties arise when interpreting such results: the reaction occurs under an ill-defined atmosphere, and buoyancy effects can be severe. This behaviour is illustrated in Table 1 showing calculations of the apparent changes in the mass resulting from substituting some of the pure carrier gases by a certain amount of hydrogen. In the cited paper [28], the atmosphere has been changed from pure argon to 25 vol% of oxygen. As emerges from Table 1, such a change in the density of the surrounding atmosphere will lead to an apparent weight gain of the order of 420 μg, assuming 1.0 ml of the total volume of sample, reference material and sample holder. Taking into account that the mass of the reactant was 50 mg, one can estimate that the artefact caused by the buoyancy has not been smaller than 10–20 μg. When interpreting the observed weight gain (46.7 μg), this fact has to be taken into consideration. Similar problems have been observed with the room-temperature reduction of PdO by conventional TA (Fig. 6). The results obtained by means of PTA demonstrates the benefit of this method.

4.3. *Very small progresses of the reaction can be investigated*

The application of this feature of PTA leads to the following advantages.

(a) Due to the small extent of the reaction occurring during the pulse, the observed thermoanalytical signals are not disturbed by the uncontrolled change in the temperature in the system caused by the heat of reaction. This is of great importance for exothermic reactions, especially at temperatures of high reaction rate, where the evolved heat can significantly influence the required temperature programme. This point causes severe uncertainties when using conventional TA. Table 2 illustrates the effect of temperature changes on the apparent weight gain for different gas atmospheres. For 50–100 mg samples, the thermal effect can alter the sample temperature by a few

Table 2

Apparent weight gains in µg resulting from a temperature increase for different gases. Total volume of the sample holder, crucibles, sample and reference material of 1 ml is assumed.

Temperature difference, °C	Ar	Air	N_2	He	H_2
1	6.6	4.8	4.7	0.6	0.3
5	32.0	23.2	22.5	3.2	1.6
10	63.0	45.8	44.3	6.3	3.2
50	275.4	200.2	193.8	27.7	13.9

degrees of centigrade, giving rise to an apparent change in the weight in the 0.2–0.6 mg range for the commonly used carrier gases. The application of PTA avoids these problems and the separation of two superimposed processes becomes possible, as has been demonstrated for the reduction of CuO, where the dehydration of the support and the reduction of alumina-supported CuO could be discriminated. The application of PTA enables the controlled progress of the reduction even at a high temperature, without accompanying significant thermal effects. The reduction in CuO studied by conventional TA at 350°C would lead to an uncontrolled rise in the temperature and, consequently, to a misinterpretation of the thermogravimetric curve.

(b) The possibility of monitoring a very small reaction progress at the desired temperatures is very important when the knowledge of the initial period of the gas–solid reaction is required, e.g. for catalytic reactions. The results of the measurements of the redox sequence in the zirconia-supported Pd catalyst (Fig. 7) were valuable in explaining the contribution of the redox mechanism to the catalytic combustion of methane.

(c) An important facet of PTA residing in the possibility of measuring small reaction extents is the differential view on the reaction, which can reveal phenomena not observable by conventional TA. Experiments with labelled solids are difficult to carry out when using conventional TA. Investigations of the methane combustion over ^{18}O-labelled zirconia-supported Pd catalysts, described in the preceding chapter, were performed with 100 mg samples of the catalyst. The oxygen content in the active phase, i.e. PdO, amounted to 3.92 wt%, corresponding to a volume of 2.74 ml of O_2. The applied flow of the gaseous reactants, containing 4 vol% of O_2, was 50 ml/min. Assuming that the system had reached the steady state after 30 min, the amount of oxygen being in contact with the catalyst was more than 20 times greater than the amount of the labelled oxygen in the catalyst. Applying the conventional TA method, the catalyst would be deprived of its ^{18}O very fast.

(d) Due to the small changes in the reaction progress, PTA enables monitoring of the changes in gas and solid phases during the course of the gas–solid reactions.

The conventional pulse method used for investigating reactions between gas and solid, e.g. catalytic reactions, enables only monitoring of changes of the gas phase. PTA additionally gives information concerning the simultaneously occurring thermal effects and weight changes caused by the investigated reaction. The simultaneous monitoring of the phenomena caused by pulses of the reactive gas gives the unique opportunity for the interpretation of the changes in the solid composition during the process. The results of the investigation of the behaviour of the Pd-catalyst during the methane combustion clearly revealed its oxidation during the course of the reaction (see Fig. 9), confirming, on the other hand, the stability of the PdO phase in this reaction (Fig. 12).

The high sensitivity of monitoring thermal effects accompanying the changes in the mass and gas compositions provides also the possibility of measuring even small effects such as adsorption–desorption phenomena during gas–solid reactions.

4.4. The exact calibration of the EGA signals can be performed

PTA enables the introduction of a well-defined amount of the gas to the system at any temperature (non-isothermal) and/or time (isothermal mode). This benefit of PTA increases its potential in investigating not only gas–solid reactions, but also decomposition of the solids. Injected pulses can be used as a reference for the quantification of the signals originating from the evolution of gas(es) formed during the reaction. Since the calibration can be done during the course of the investigated reaction, its accuracy is significantly greater compared to off-line calibration methods. The influence of all settings, determined by the construction of the apparatus and the experimental parameters, resulting in a change in the intensity of the EGA response, does not obscure the results. Its contribution to the transformation of the input (amount of analyzed species) to the output signal (observed intensity) is the same for both responses: the first, originating from the injection and the second, from the reaction. This conclusion is valid only when the calibration factor does not depend strongly on temperature (compare with [25]). As emerges from the corresponding results presented in Fig. 13, the influence of temperature on the sensitivity of the mass spectrometric signals is negligible, or at least not greater than the accuracy of the MS signals, amounting to ca. 2–3%.

The possibility of the exact calibration of the MS signal by means of PTA increases significantly the potential of the coupled TA–MS method. The determination of the content of certain species in the investigated system by this method has significant advantage compared to conventional elemental analysis measurements. From conventional microanalysis, only the total amount of analyzed species can be measured, and it is also impossible to resolve the species evolved in multistage reactions or to determine very small amounts of the products. As emerges from the results presented in Fig. 14, the application of PTA enables the determination of very small amounts of the organic residues evolved from the solid, as demonstrated for the zirconia aerogel during its crystallization. The applied method allowed to distinguish the signals having the ratio of the intensities as low as 1 : 300 (the carbon content evolved during crystallization that amounted to 0.007 wt% vs. the carbon content evolved during combustion that amounted to 1.9 wt%). The possibility of injecting the pulse, used later for the calibration, at any moment of the investigated reaction, increases significantly the accuracy of the quantification of the recorded MS signals. The applied method can also be used in the quantification of the signals obtained by means of other methods, e.g. GC or FTIR.

5. Conclusions

The novel PTA method broadens the application of the conventional thermoanalytical methods for investigating the gas–solid reactions and the decomposition of solids. The main benefits of the new method are:

1. The possibility of monitoring gas–solid processes with specific extent of the reaction at desired temperatures. The reactions can be stopped at any point between the pulses, enabling elucidation of the relationship between the composition of the solid and the reaction progress.
2. The opportunity of carrying out the measurement at appropriate temperatures allows the separation of the simultaneously occurring reactions and minimizes the influence of the undesired buoyancy effect.
3. Monitoring of the simultaneous changes in mass, thermal effects, composition and amount of gaseous reactants and products under pulse conditions is possible. This property enables collecting simultaneous information concerning the behaviour of the gas and solid phases.
4. Injection of a known amount of gas into the system during measurement allows a more reliable quantitative calibration of the MS signal, reaching an accuracy for the evolved species below 0.01 wt%.

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