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PULSE THERMAL ANALYSIS
A new range of opportunities*

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Abstract

Pulse thermal analysis (PTA) is based on the injection of a specific amount of gaseous reactant into a carrier gas stream. PTA provides the following advantages compared to conventional TA: (i) quantitative calibration of the mass spectrometric signals allows increasing the sensitivity of TA measurements; (ii) monitoring of gas-solid processes with defined extent of reaction i.e. the reaction can be stopped at any point between pulses, enabling elucidation of the relationship between the composition of the solid and the reaction progress; (iii) simultaneous monitoring of changes in mass, thermal effects, composition and amount of gaseous reactants and products under pulse conditions.

Keywords: pulse thermal analysis, thermal analysis combined with mass spectrometry

Introduction

Pulse thermal analysis (PTA) is based on the injection of a specific amount of gaseous reactant into a carrier gas stream while monitoring changes in mass, enthalpy and gas composition resulting from the incremental reaction extent [1]. In contrast to conventional thermal analysis (TA) and all its modifications, the course of the reaction is controlled not only by temperature but also by transient change in the composition of the reactive atmosphere.

PTA offers three principle opportunities of thermoanalytical studies, depending on the kind of injected gas: (i) injection of an inert gas, facilitating quantitative calibration of the mass spectrometric signals, allows to increase the sensitivity of TA measurements to such an extent that species in amounts lower than 0.01 wt% can be detected; (ii) injection of a gas which reacts with the solid sample provides the op-

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portunity of investigating all types of gas-solid reactions; and, (iii) injection of a gas which adsorbs onto the sample surface facilitates the study of adsorption phenomena under atmospheric pressure and at the particular temperature.

Here we briefly demonstrate the range of new opportunities, PTA offers using examples from our work in material science and catalysis.

Experimental

Experiments were carried out isothermally or non-isothermally (applied heating rates were generally in the range of 5–10 K min^{-1}) on a Netzsch STA 409 simultaneous thermal analyzer equipped with a gas pulse device (Netzsch) that enables injection of controlled amounts of two different pure gases or gaseous mixtures into the system. The amount of injected gas could be set from 0.01 to 10 ml. Primarily, volumes of 0.25, 0.5 and 1.0 ml were used. Gases evolved during the reaction and/or injected into the system were monitored on-line with a Balzers QMG 420 quadrupole mass spectrometer connected to the thermal analyzer by a heated (ca. 200°C) capillary.

Results

Relation between TA and MS signals in PTA

The most distinct feature of PTA is the fact that changes of the gaseous atmosphere during experiments occur in a limited, short period of time after each injected pulse of the desired gas. When relating TA and MS signals in PTA several aspects influencing the transfer of the injected species in the carrier gas and to the solid sample have to be considered. Depending on fixed parameters of the thermoanalytical system, such as injection position, volume of the heating chamber, direction of the gas flow and variable parameters such as kind of carrier gas and its flow rate and the amount and kind of injected gas, the mass spectrometric signal, due to the injected species, changes its shape. A detailed study of the influence of mass transfer on the relation between thermoanalytical and mass spectrometric curves in a combined TA-MS system has been reported recently [2]. Cumulative distributions of the MS signals of an oxygen pulse injected into two different carrier gases (He, Ar) at room temperature is presented in Fig. 1A. The higher molecular diffusion coefficient of the injected gas in helium as compared to argon, significantly changes the time for the disappearance of the MS signal. The curves in Fig. 1A indicate that 75% of the injected oxygen flows through the chamber in 3.2 min when the carrier gas is Ar, whereas 4.2 min elapse with He. At higher temperatures (Fig. 1B) the MS signals become narrower, but their areas remain constant (see inset in Fig. 1B). The change of the peak shape at higher temperatures is caused by the different temperature dependence of the convectional and diffusional flow properties of the carrier gas, giving rise to a change of the transportation of the injected molecules into the carrier gas [3]. The transient character of the pulse technique offers interesting opportunities for PTA applications which will be illustrated in the following examples.

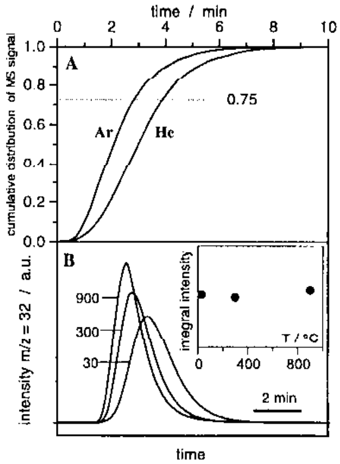


Fig. 1 Influence of different diffusivities of injected gas in carrier gas on MS signal: A) Response MS signal (cumulative distribution) on oxygen pulse (1 ml) injected at room temperature into Ar and He carrier gas (50 ml min^{-1}), respectively. B) Shape of the MS signals as a function of temperature (marked in centigrade on the curves). Inset presents the temperature dependence of the integral intensities

Opportunities of PTA

Injection of an inert gas

The opportunity of injecting a known amount of any gas into the carrier gas stream provides a qualitative calibration by relating the MS signal to injected quantity of probe gas. Previously published results [3, 4] indicate that the kind of the carrier gas and temperature do only affect the shape of the MS signal but not its integral intensity. The application of PTA for the quantitative calibration of MS signals is illustrated by comparing results obtained by means of thermogravimetry and a simultaneous PTA-MS experiment (Fig. 2). 4.62 mg of $CaCO_3$ was decomposed under helium with a heating rate of 10 K min^{-1}, the observed mass loss (Fig. 2A) amounted to 2.02 mg, which agreed well with the stoichiometric value of 2.03 mg. In order to quantify the mass spectrometric signal of *m/z*=44, two 1 ml pulses of CO_2 were injected before and after the decomposition of calcium carbonate (Fig. 2B). The mean value of the integral intensities of the injected pulses was 1.96 a.u., the integral intensity of the signal of evolved CO_2 was 2.95 a.u. The temperature of the injected gas was 28.5°C. The amount of CO_2 formed during $CaCO_3$ decomposition calculated from these data corresponds to 2.01 mg, confirming the accuracy of the quantification method.

The application of the MS curve for the quantification of thermoanalytical results seems to be unnecessary when the reaction proceeds in well resolved step(s) and the stoichiometry and composition of the reactant and product(s) are already

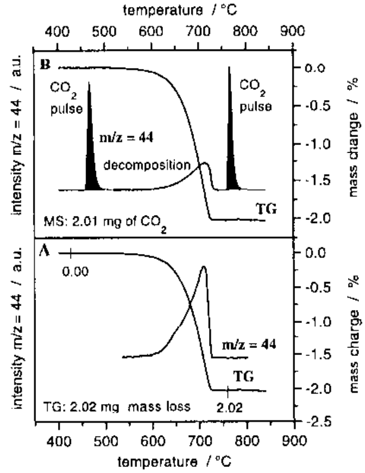


Fig. 2 A) Thermogravimetric and B) mass spectrometric determination of the amount of CO_2 evolving during decomposition of calcium carbonate. The 1 ml pulses of CO_2 were used for the calibration of the MS signal

known as in the presented example of $CaCO_3$ decomposition. In practice, this obvious remark is not fully correct as the example below of the decomposition of silver carbonate illustrates.

The mass loss of 21.66% recorded during Ag_2CO_3 decomposition (Fig. 3) agrees very well with the stoichiometric course of this reaction which occurs in two consecutive steps affording a total mass loss of 21.76%.

$$Ag_2CO_3 \rightarrow Ag_2O + CO_2 \rightarrow 2Ag + 0.5O_2 \qquad (1)$$

The quantification of the MS curves by injecting 1 ml pulses of CO_2 and O_2 (not shown) indicated that the analyzed carbonate had the proper stoichiometric composition (CO_2 content: stoichiometric 15.95 wt%, found 15.9%, oxygen content: stoichiometric 5.80 wt%, found 5.7%). However, the deconvolution of the m/z=44 signal indicates that ca. 25% of the total amount of CO_3^{2-} ions remain in the product after the first stage of the decomposition and is not evolved before the total decomposition to metallic silver occurs. The results show that the usual method of silver oxide synthesis, consisting of the decomposition of silver carbonate, can lead to the formation of Ag_2O which contains significant amounts of carbon dioxide that were not removed from the oxide before its decomposition.

The quantitative interpretation of the TG curve is even more uncertain when the temperature ranges of the various decomposition stages, particularly in multicomponent systems, overlap each other. Also, when the mass change is below 1–2 wt% due to the low content of the reacting phase, its quantitative interpretation is difficult due to the contribution of the buoyancy effect.

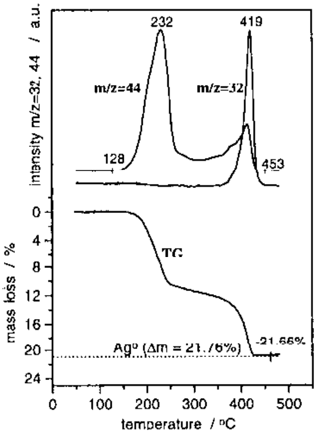


Fig. 3 Thermal decomposition of the silver carbonate to metallic silver (heating rate 10 K min^{-1}, helium, 50 ml min^{-1})

Figure 4 depicts the oxidation of graphite present in minor amounts in a mixture with γ-alumina. The evolution of CO_2 is superimposed onto the continuous mass loss due to the evolution of water from the alumina and this makes the determination of the carbon content from TG curve very inaccurate. The determination of the carbon content based on the quantitative interpretation of the MS signal, after its calibration by five pulses of CO_2, indicated the high accuracy of this procedure despite the low concentration of the analyzed phase: the real content of graphite in the mixture was 0.09%, the measured amount was 0.08%.

The high sensitivity of mass spectrometry enables the determination of evolved species even when their concentration does not exceed 0.01 wt%. Determination of such small quantities is rather impossible using standard TA-techniques. Results of the determination of organic residue present in ZrO_2 aerogel [1, 5] show that it is possible to measure the very low amount (0.007 wt%) of carbon released during the crystallization of zirconia. This high sensitivity of analysis, being one of benefits of PTA, it is further illustrated below by the results of the quantification of the evolved gases during TA-MS measurement of a cuprate superconductor of the $Y_2Ba_4Cu_{6+n}O_{14+n}$ family [6]. These superconductors often contain a remarkable quantity of carbon dioxide which can strongly influence their properties. In the studies of carbon dioxide incorporation into the superconductor crystal lattice, the primary question is whether it is possible to remove CO_2 from the superconductor by heating it without decomposing. Also, the knowledge of oxygen substitution by CO_3^{2-} helps understanding the properties of YBaYCuO and therefore can be valuable in the preparation of these materials.

The MS signals due to oxygen and CO_2 evolution, recorded during the superconductor calcination under argon, are presented in Fig. 5. The 1 ml pulses of CO_2, used later for the calibration, were injected before the carbon dioxide release which starts

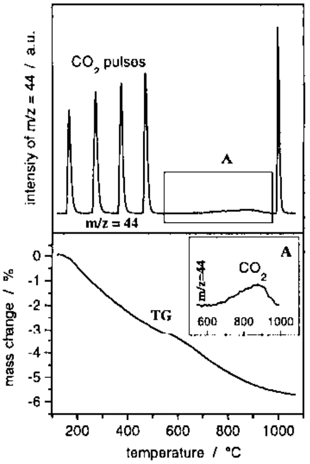


Fig. 4 TG and MS traces of the combustion of the graphite mixed with γ-alumina. Inset A presents the magnification of *m/z*=44 signal. CO_2 pulses injected before and after combustion of graphite were used for the MS curve calibration (10 K min^{-1}, oxygen 20 vol%, balance He, total flow 50 ml min^{-1})

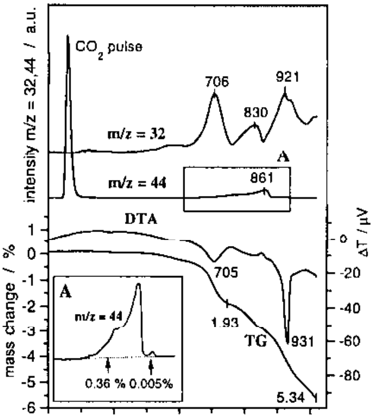


Fig. 5 Calcination of the YBaCuO superconductor in argon. Inset A presents the evolution of CO_2 occurring above 600°C. The 1 ml pulse of CO_2 was used for calibration of the *m/z*=44 signal

at ca. 600°C. The magnification the MS signal due to CO_2 release (inset A) is shown in the lower part of Fig. 5. As the results indicate, the application of the PTA method made it possible to quantify two steps of CO_2 evolution, determine their temperature ranges and to distinguish signals with intensity ratios as low as 1:70 (0.36 *vs.* 0.005 wt%). MS signals clearly indicate that evolution of carbon dioxide occurs at temperatures higher than that of superconductor decomposition, this is reflected by the temperature at the beginning of oxygen evolution.

Injection of a gas reacting with the solid

PTA allows to dose the reacting gas in small quantities facilitating the study of gas-solid reactions in differential mode. The reaction between injected gas and the solid occurs only during the duration of the pulse. This feature provides several new opportunities for investigating of gas-solid reactions as e.g. the preparation of solids with well specified extend of the reaction. Depending on the temperature and pulse volume, any required reaction progress can be reached. The stepwise reduction of CuO by hydrogen and the concomitant characterization of the phase composition of the intermediate products was described in [1]. Here this feature of PTA is illustrated by the study of the reduction of manganese oxides by CO. The redox transformations possible for the system Mn–O at temperatures above 500°C are shown in Scheme 1. In order to compare the catalytic activity of Mn_2O_3 and Mn_3O_4 in the oxidation of CO, the characterization of the redox behaviour of these oxides was carried out using the PTA method. The course of the reduction of Mn_2O_3 by 1 ml pulses of CO injected at 500°C is depicted in Fig. 6. The aim of this investigation was to check whether pure Mn_3O_4 is formed when the stoichiometric mass loss of 3.38% is reached during the reduction process (Scheme 1). The phase composition of the products was checked after 2, 6 and 12 pulses, which afforded the samples labelled as 1, 2 and 3, respectively. The XRD patterns presented in the lower part of Fig. 6 indicate that sample 3, corresponding to the stoichiometric mass loss for reduction

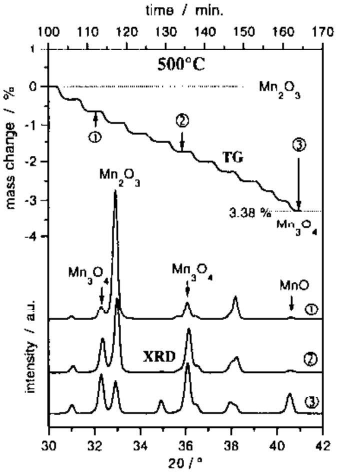
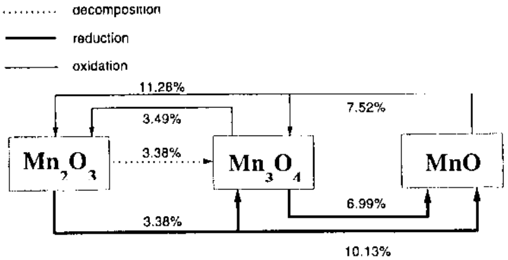


Fig. 6 Stepwise reduction of Mn_2O_3 by pulses of CO (1 ml) and XRD patterns of the products corresponding to different extends of reduction, taken at the points marked by 1, 2, and 3, respectively

of Mn_2O_3 to Mn_3O_4 contains three phases: Mn_2O_3, Mn_3O_4 and MnO. Even at very low degree of reduction (sample 1, mass loss 0.67 wt%), MnO containing only Mn (+2) already forms. The preparation of samples corresponding to such a low and well defined reaction progress, is rather impossible by any conventional, iso- or non-isothermal TA technique.



Scheme 1 Possible redox transformations with the related mass changes in the system Mn–O at temperatures above 500°C

Another interesting feature of PTA is its suitability for investigating complex reaction systems at any desired temperature. Artifacts caused by temperature settling are omitted which facilitates better distinction of concomitantly occurring processes. This feature is illustrated by a study of the reduction of the supported IrO_2. The determination of mass loss due to oxide reduction is impossible in a conventional TA run as shown in Fig. 7. The mass loss due to removal of the water produced during the reaction overlaps with the mass loss due to the desorption of the water from the support. The exact determination of the IrO_2 content is possible by means of PTA. After total desorption of the water from the support at 200°C, the observed mass loss

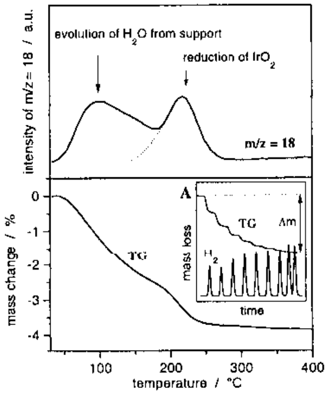


Fig. 7 Reduction of supported IrO_2 carried out by means of conventional TA (10 K min^{-1}, H_2 20 vol%, balance He, total flow 50 ml min^{-1}) and PTA (200°C, *iso*-), respectively. The mass loss due to hydrogen pulses (1 ml, PTA experiment, inset A) results from the reduction process only

Δm caused by hydrogen pulses (see inset in Fig. 7) can only originate from the reduction of iridium oxide. The iridium content determined by this method (4.98 wt%) agrees well with the nominal loading of the catalyst which amounted to 5.00 wt%.

Another opportunity of PTA is its potential to investigate processes with differential steps in reaction extent. Due to the simplicity of pulsing different pure gases or gaseous mixtures, PTA can be a useful tool for examining e.g. redox processes which occur on solids during catalytic processes. The application of PTA for investigating the redox behavior of Pd/ZrO_2 catalysts [7] during the catalytic combustion of methane, provided important information concerning the composition of the catalytically active phase and the reaction mechanism. Such a differential characterization of the reaction progress is illustrated by the investigation of the redox properties of different CeO_2 samples [8]. The redox behaviour of this oxide, i.e. the ease of its reduction and reoxidation, distinctly influences its application as an oxygen buffer during catalytic reactions. The difficulty in applying conventional TA techniques for investigating such phenomena is caused by the fact that only very small changes of the composition of ceria occur during catalytic process. The composition of the sample only slightly change due to subsequent reduction and reoxidation cycles, and, consequently, the characterisation of the reducibility of ceria by investigating the total reduction process is of little value.

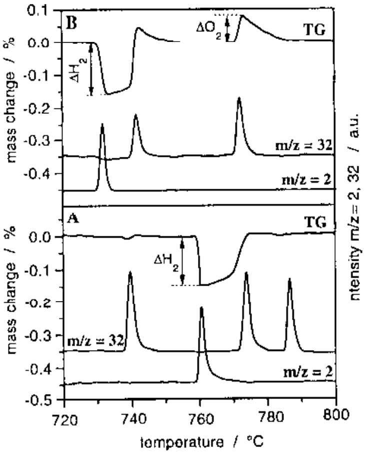


Fig. 8 The changes of the mass due to the 1 ml hydrogen and oxygen pulses for conventional (A) and mesoporous (B) CeO_2, heating rate 1 K min^{-1}, carrier gas He, 50 ml min^{-1}

Two samples of ceria (Fig. 8), were reduced by pulses of hydrogen. Each pulse of hydrogen was followed by pulse of oxygen, which reoxidized the partly reduced cerium oxide. Figure 8A depicts the changes of the mass due to H_2 and O_2 pulses for the conventionally prepared sample. The second, mesoporous sample prepared using template-assisted synthesis (Fig. 8B) showed significantly higher reducibility at the same temperatures. The change of the composition from $CeO_{2.00}$ to $CeO_{1.99}$ for the mesoporous sample occurs at temperatures ca. 90 K lower than for the conventional sample. Both samples exhibited also different behaviour after oxygen pulsing. With the mesoporous sample, a distinct oxygen uptake was observed, reflected by a mass gain exceeding the mass loss due to reduction. After ca. 15 min, the excess oxygen desorbed from the ceria and the sample mass returned to its initial value. The investigations revealed the remarkable enhancement of the oxygen storage/release capacity of this sample.

Injection of a gas which adsorbs on the solid

Due to simultaneous monitoring of changes of mass and thermal effects, PTA can be applied for investigating adsorption phenomena occurring under atmospheric pressure. An example showing the adsorption of ammonia at 200°C on HZSM-5 zeolite is presented in Fig. 9A. The irreversible adsorption (chemisorption) occurs during the first three pulses. Part of the ammonia adsorbed during the fourth pulse desorbs after ca. 50 min, indicating that both reversible (physisorption) and irreversible adsorptions occurred on the zeolite surface. The course of the TG curve after the last (fifth) pulse is characteristic for the physisorption process, after ca. 70 min the sample mass returns to its initial value before pulsing, indicating total desorption of the ammonia. In experiments with lower amount of sample (Fig. 9B), chemisorption of ammonia occurs only during the first pulse. The observed exothermal effect in the DTA curve, in conjunction with the mass gain resulting from the NH_3 chemisorption, allows the determination of the heat of adsorption per mole of adsorbed ammonia. The second and third ammonia pulses led to reversible adsorption. Note the relatively rapid mass loss after ammonia physisorption and the endothermic process caused by the ammonia desorption. Decreasing the pulse volume gives access to the determination of the differential heats of the adsorption.

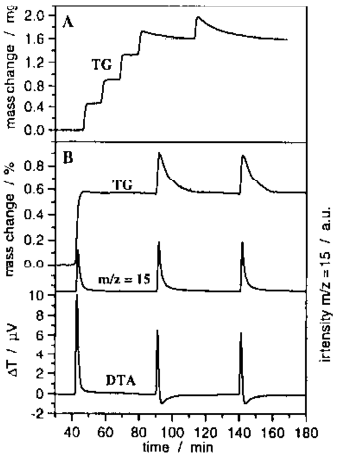


Fig. 9 The adsorption of ammonia (1 ml pulses) on HZSM-5 zeolite at 200°C. Mass of zeolite after drying *in situ* at 500°C: A) 219.91 mg, B) 30.11 mg

The described method for adsorption studies was used in our laboratory for the investigation of the adsorption of the ammonia on zeolites [9], silica-titania aerogels [10], V_2O_5/TiO_2 [11], ammonia and carbon dioxide on Co-Fe phases [12], and adsorption of oxygen, carbon monoxide and carbon dioxide on Au/TiO_2 [13].

Conclusions

PTA extends the versatility of conventional thermoanalytical methods by providing the means for studying small reaction progresses. PTA combines this advantage with all the opportunities offered by TG, DTA and MS. Advantageous features of PTA are:

– Injection of a known amount of gas into the system during measurement allows quantitative calibration of the MS signal which greatly increases the opportunities of thermoanalytical investigations, especially for the analysis of multicomponent systems. Sensitivities below 0.01 wt% can be achieved for the evolved species.

– Monitoring gas-solid processes corresponding to a specific extent of reaction at desired temperature is possible. The reaction can be stopped at any point between pulses, enabling elucidation of the relationship between the composition of the solid and the reaction progress.

– The potential to monitor simultaneous changes in mass, thermal effects, composition and amount of gaseous reactants and products under pulse conditions. This feature enables to gain simultaneously information concerning both gas and solid phases.

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