POTENTIAL OF THERMAL ANALYSIS IN PREPARATION AND CHARACTERIZATION OF SOLID CATALYSTS

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Abstract

Supported catalysts contain often only small amounts of active component(s) which renders their characterization difficult, particularly because they usually contain a substantial amount of water. Thermal analysis (TA) coupled with mass spectrometry (MS) offers an interesting potential for characterizing such material, various steps of catalyst preparation as well as crucial properties of fresh and used catalysts can be investigated. Some examples illustrating the versatility of TA-MS in catalysis research, such as solid-state reactions occurring upon exposure of the precursors or catalysts to reducing, oxidizing or inert atmosphere, are presented in this study. The combined use of TA and MS allows in many cases a much more detailed interpretation of the observed phenomena than could be achieved by one of these methods alone.

Introduction

Knowledge of the relationship between preparation method and resulting structural and catalytic properties of solids is a necessary requirement for catalyst design. Although heterogeneous catalysis occurs on the surface, bulk properties as they are investigated by thermal analysis provide useful information concerning the relationship between preparation conditions and structural and chemical properties of solid catalysts.

In the case of multicomponent systems containing a small amount of the investigated phase, such as supported catalysts where often only a few percents of the active components are present, it is important to combine thermal analysis (TA) with analytical methods monitoring the evolved gases as e.g. mass spectromertry (MS). The simultaneous analysis of the evolved gases identifies of species which evolve during thermal treatment, aids in interpreting the observed changes of mass or enthalpy, and results in an increase of sensitivity concerning chemical changes. As it will be shown in this study, analysis of the components in multi-phase systems, being present in amounts below 0.5 wt%, can be resolved. The aim of this study is to

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illustrate the potential of TA coupled with MS for preparation and characterization of catalysts.

Experimental

Thermoanalytical measurements were carried out on a Netzsch STA 409 thermoanalyzer using α-alumina as a reference. Gases formed during thermoanalytical runs were monitored with a Balzers QMG 420 mass spectrometer. The heating rate used was generally 10 K min^{-1}, only for the oxidation of the amorphous alloys 5 K min^{-1} was applied. X-ray diffraction pattern of the samples were measured using a Siemens D5000 powder diffractometer and CuK$_\alpha$ radiation.

Results and discussion

### Application of thermal analysis in catalyst preparation

The application of TA for elucidating the solid-state transformations occurring during catalyst preparation is illustrated using two vastly different methods applied for preparing copper/zirconia catalysts.

A) copper/zirconia prepared by coprecipitation

Copper/zirconia prepared by coprecipitation of corresponding metal nitrates is an efficient catalyst for the synthesis of methanol from carbon dioxide and hydrogen [1]. After precipitation catalyst are dried at 120°C, then calcined, resulting in copper oxide/zirconia, and finally reduced by hydrogen before use. The calcination process should be performed in the optimal temperature range providing the desired catalyst properties. Generally it is necessary to remove water from hydrated oxides and hydroxides, which form after precipitation from aqueous nitrate solutions, and to decompose the nitrate species present in the catalyst precursor. This thermal treatment has to be carried out under conditions, where neither drastic loss in the surface area nor undesired segregation and crystallization occurs. The results of the TA investigations of a Cu/zirconia catalyst are presented in Fig. 1. The TA and MS curves indicate that a calcination temperature exceeding 500°C is necessary to remove residual NO_3^- species and water present in the dried precipitate. However, a temperature higher than ca. 570°C is disadvantageous due to crystallization of the amorphous ZrO_2, occurring in the range 580–615°C with a maximum at 608°C.

B) Metal/zirconia catalysts prepared by oxidation of glassy metal/zirconium alloys

Another method for preparing copper/zirconia catalysts, highly active for methanol synthesis, is the oxidation of glassy CuZr alloys. This preparation method has been applied for various metal/zirconia catalysts (see e.g. Baiker [2] and references cited therein). The most common procedure for producing glassy metals (amorphous metal alloys) is rapid quenching of the liquid constituents of the alloy with cooling rates exceeding ca. 10^5 K min^{-1}. Metallic glasses are amorphous and
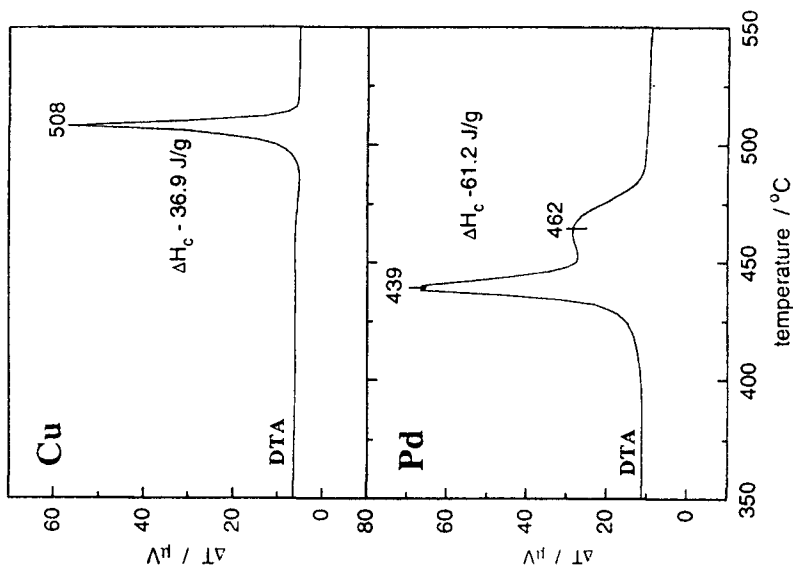
Fig. 2 Crystallization behaviour of amorphous $Cu_{70}Zr_{30}$ (Cu) and $Pd_{33}Zr_{67}$ (Zr) alloys under argon studied by DTA
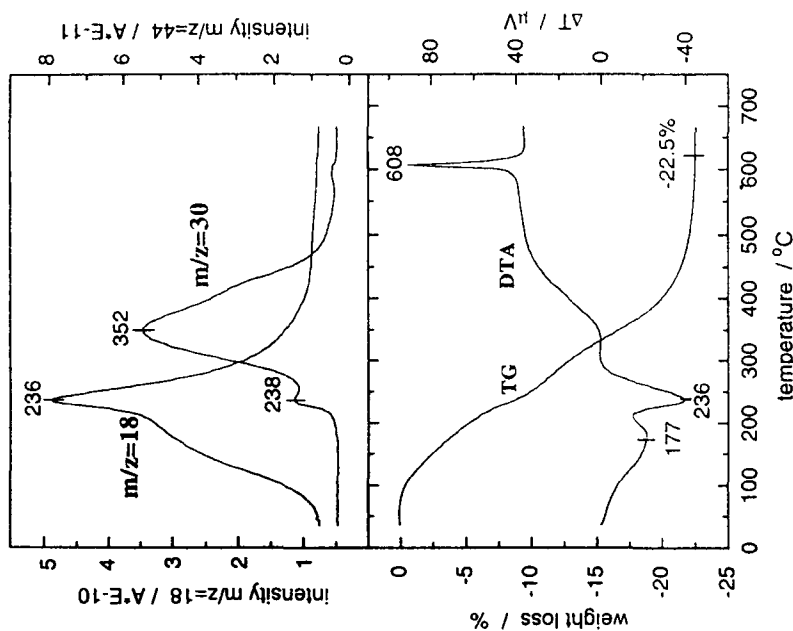
Fig. 1 Calcination of a Cu/zirconia catalyst in air investigated by means of TA-MS

metastable. Under certain conditions (heat, pressure, atmosphere etc.) the undergo various solid-state transformations, such as crystallization, phase segregation and agglomeration.

In previous investigations we have shown [3–7] that highly active catalysts can be prepared from glassy metals by either controlled oxidation of the alloy in air or by in-situ oxidation, which is possible if the catalytic reaction is performed under an oxidizing atmosphere (e.g. CO or CH_4 oxidation). Catalysts derived by oxidation of amorphous alloys were shown to exhibit often higher activity than corresponding catalysts with the same composition, but prepared by conventional preparation methods, such as impregnation or coprecipitation. Thus, the controlled transformation of glassy metal alloys is an interesting alternative to the classical preparation methods.

During this transformation the following processes can occur: crystallization of the amorphous alloys, oxidation of constituents by gas–solid and solid–solid reaction and segregation. Thermoanalytical investigations of these reactions are illustrated using as examples the oxidations of $Pd_{33}Zr_{67}$ and $Cu_{70}Zr_{30}$ amorphous alloys. DSC curves of the crystallization of $Pd_{33}Zr_{67}$ and $Cu_{70}Zr_{30}$ alloys in inert gas atmosphere (argon) are presented in Fig. 2. Under the conditions used, crystallization occurs in the ranges 490–518°C ($Cu_{70}Zr_{30}$) and 406–495°C ($Pd_{33}Zr_{67}$) with these alloys. The two stages discernible in the crystallization of $Pd_{33}Zr_{67}$ were also observed by Cantrell et al. [8]. The specific heats of crystallization determined from DSC measurements amount to 36.9 J/g ($Cu_{70}Zr_{30}$) and 61.2 J/g ($Pd_{33}Zr_{67}$), respectively.

The results of the thermoanalytical investigations of the oxidation of both alloys are shown in Fig. 3. TG curves indicate that the oxidations start already at temperatures significantly lower (ca. 220°C with $Cu_{70}Zr_{30}$ and ca. 300°C with $Pd_{33}Zr_{67}$) than the corresponding crystallization temperatures of the amorphous alloys. Under the conditions used, total oxidation is reached at ca. 720°C with $Cu_{70}Zr_{30}$, and ca. 670°C with $Pd_{33}Zr_{67}$, respectively. The exothermal oxidation, as indicated by the simultaneously measured DTA curves, occurs in two descernible steps with $Pd_{33}Zr_{67}$, and a single prominent step with $Cu_{70}Zr_{30}$. At higher temperatures, the products of the oxidation, CuO and PdO, respectively, decompose. Decomposition in air starts with CuO at 1031°C, and with PdO at 802°C. The other product formed upon oxidation, ZrO_2, is stable up to higher temperature and melts (after some polymorphic transformations) at 2680°C.

X-ray diffractometry (XRD) combined with thermoanalytical measurements was used to gain information about the bulk structural changes occuring during oxidation of the amorphous alloys. We found that the reaction of the alloy constituents with oxygen is superimposed by solid-state reactions, which influence the chemical and structural properties of the final catalysts. PdO and CuO, formed during the first stage of the oxidation, are reduced by the metallic zirconium, present in the unoxidized core of the amorphous alloy, to metallic Pd and Cu_2O (or even Cu), respectively.

In order to examine these reactions, $Pd_{33}Zr_{67}$ and $Cu_{70}Zr_{30}$ were oxidized isothermally on the thermobalance to different degrees of oxidation α (α is defined as
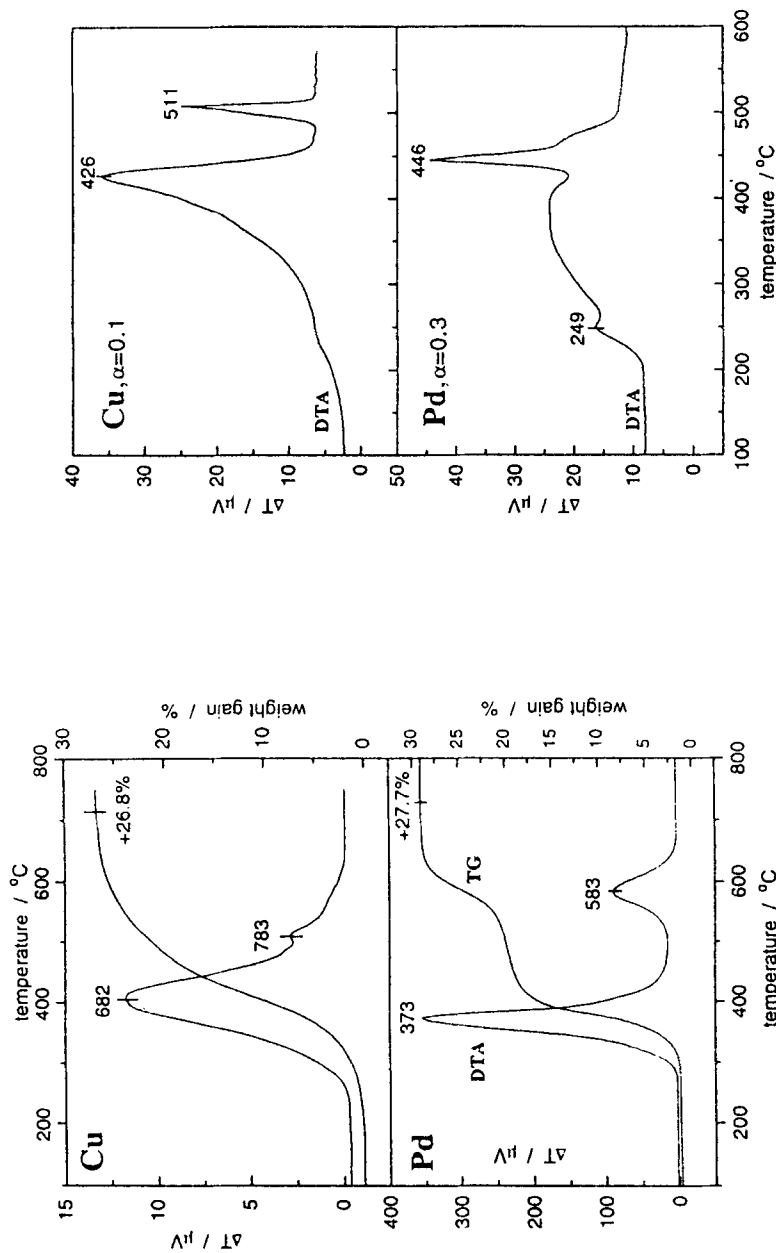
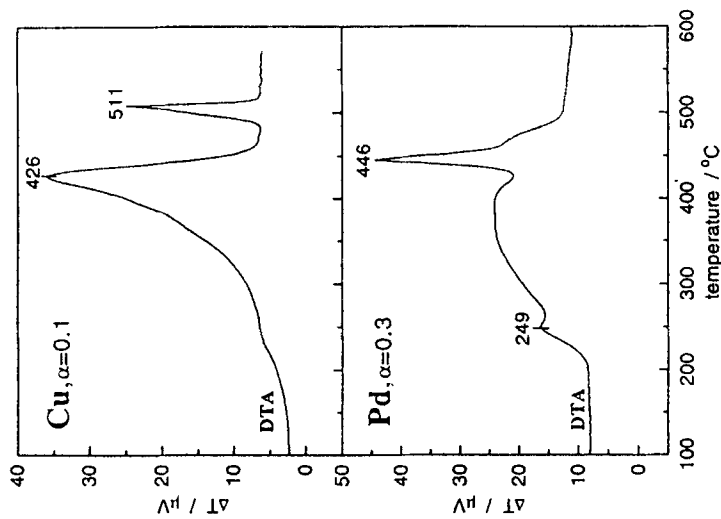**Fig. 4** Solid state reduction of partially oxidized $Cu_{70}Zr_{30}$ (Cu) and $Pd_{33}Zr_{67}$ (Zr) alloys investigated by DTA under Ar. Before measurement $Cu_{70}Zr_{30}$ was oxidized to $\alpha = 0.1$ (definition of α is given in text) and $Pd_{33}Zr_{67}$ to $\alpha = 0.3$

Fig. 3 Oxidation of amorphous $Cu_{70}Zr_{30}$ (Cu) and $Pd_{33}Zr_{67}$ (Zr) alloys in air studied by DTA and TG

the amount of oxygen consumed in the oxidation divided by the amount of oxygen necessary to oxidize the alloy's constituents completely to CuO, PdO and ZrO_2). Subsequently, the oxidized samples were rapidly cooled to room temperature and then subjected to TA measurements under inert gas atmosphere. Figure 4 depicts the DTA curves measured for $Cu_{70}Zr_{30}$ previously oxidized to $\alpha = 0.1$ and $Pd_{33}Zr_{67}$ oxidized to $\alpha = 0.3$. The DTA curves show broad signals arising from solid-state reductions of CuO and PdO, formed at the beginning of the oxidation. These signals arising from the reduction of the oxides by metallic zirconium are superimposed at higher temperatures by peaks, attributed to the crystallization of the unoxidized part of the amorphous alloys ($511^{\circ}C$ with $Cu_{70}Zr_{30}$ and $446^{\circ}C$ with $Pd_{33}Zr_{67}$, respectively). Note the similarity of these peaks to the crystallization peaks for unreacted alloys presented in Fig. 1. XRD analysis of the alloys after oxidation to $\alpha = 0.1$ ($Cu_{70}Zr_{30}$) and $\alpha = 0.3$ ($Pd_{33}Zr_{67}$) indicated the presence of CuO and PdO. After the solid-state reduction (TG curves showed no significant change of the sample weights), PdO was fully reduced to Pd, and CuO to a mixture of Cu_2O and Cu. Detailed studies, reported by Baiker et al. [5], confirmed that at low temperatures the solid-state reduction of the initially formed oxides by metallic zirconium is faster than the rate of gas-solid oxidation. With increasing degree of oxidation α, the concentration of metallic Zr decreases and the solid-state reaction becomes too slow to influence significantly the ratio between metallic Pd or Cu and their corresponding oxides.

The above results demonstrate the potential of thermal analysis in elucidating the relevant transformations occurring in the preparation of metal/zirconia catalysts by oxidation of amorphous alloys. The knowledge gain concerning the temperature ranges, where crystallization occurs and oxidation starts, allowed to adjust properly the temperature for isothermal oxidation avoiding sintering and concomitant decrease of the surface area of the final catalysts.

Application of thermal analysis for catalyst characterization

Thermal analysis can be used for the determination of the amount of the active phase present in the catalyst before and after use in the catalytic reaction. It is especially useful for investigating supported systems with high surface area, where due to the large amount of absorbed water, the use of other analytical methods can cause severe problems or even rule out an exact compositional analysis. For illustration we shall consider the determination of: A) the copper content of a copper/alumina catalyst; B) the V_2O_5 loading of a supported vanadia catalyst; and, C) the amount of organic impurities in catalysts produced by the sol-gel method.

A) Copper content of coprecipitated copper/alumina catalyst

The determination of the active copper phase in copper/alumina catalysts used for the synthesis of methylamines from CO_2, H_2 and NH_3 [9] is difficult due to the large amount of water present in these catalysts after preparation. Catalysts with high Cu loadings (ca. 30 and ca. 50 wt% of CuO) were prepared by mixing a slurry
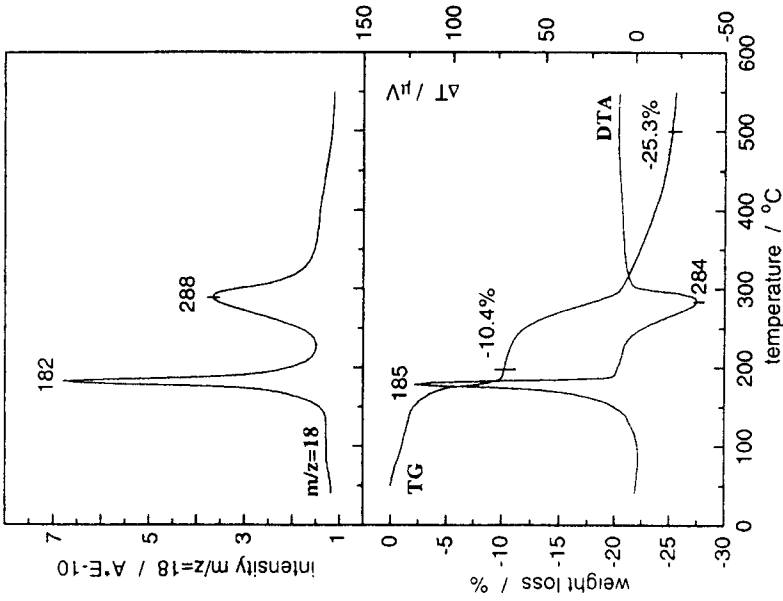
Fig. 6 Reduction of supported CuO/alumina catalyst (same sample as in Fig. 5) under 80 vol% hydrogen, balance argon
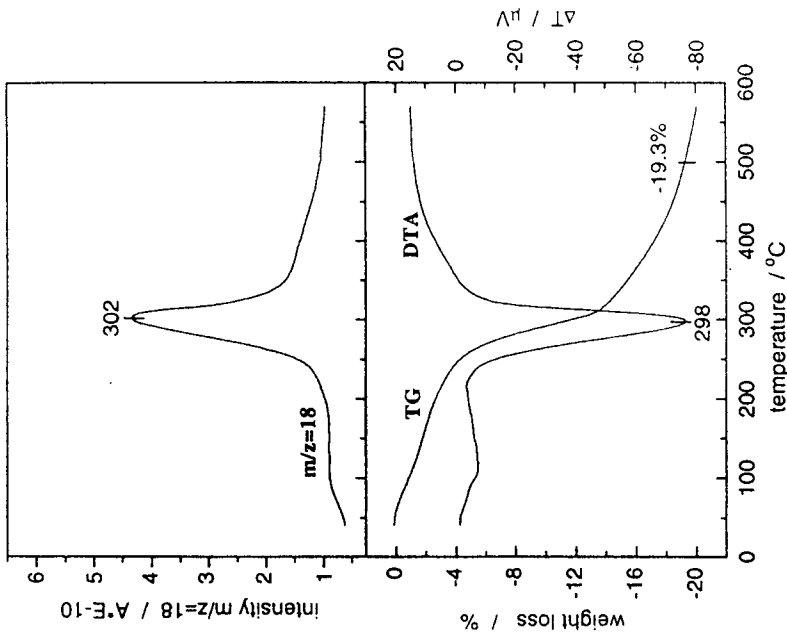

Fig. 5 Heat treatment of supported CuO/alumina catalyst under argon studied by TA-MS

of aluminium hydroxide gel in an aqueous copper nitrate solution with a solution of potassium hydroxide at 80°C. The resulting precipitates were aged for 30 min, filtered, washed and dried at 150°C for 6 h. In spite of these rather rigorous drying conditions, the dried catalysts contained a considerable amount of water. TA-MS measurements of the sample containing ca. 30 wt% of CuO are depicted in Fig. 5. The TG curve clearly indicates that water evolution was not complete even at temperature as high as ca. 600°C. This behaviour causes severe uncertainties in determining the weight fraction of the copper phase in the sample. Thermal analysis was used to resolve this problem. The amount of copper was determined by performing measurements under inert and reducing atmosphere. This copper determination is independent of the water content. Figure 6 shows the results of the measurements (TG, DTA, MS) carried out under a hydrogen atmosphere. From the difference between the measured weight losses under Ar and H_2 one can extract the weight loss due to the reduction of CuO, and consequently the copper content. Note also the exo-peak (DTA) resulting from this reaction with a maximum at 185°C, superimposing the endothermic dehydration of aluminium hydroxide.

B) Vanadia loading of supported vanadia catalyst

The determination of the V_2O_5 content in titania supported vanadia catalysts was carried out in our laboratory in the frame of an international programm dealing with the characterization of supported vanadia catalysts (Eurocat Oxide Group [10]). The vanadia loading of a specific sample was derived from Temperature Programmed Reduction (TPR) measurements [11] and compared to that determined by TA. The loading of V_2O_5 determined by TPR in the different laboratories varied from 7.3 to 7.7 wt%.

TPR with hydrogen [12] is a widely used technique for the characterization of reducible solids and catalysts. The total hydrogen consumption can be used to quantify the reducible component of the sample if reduction of V_2O_5 to V_2O_3 is assumed. In order to compare the accuracy of TPR and TA, the vanadia content was determined by monitoring the weight loss during reduction. The results obtained by means of TA are shown in Fig. 7. The mass spectrometric curves of H_2 consumption ($m/z = 2$) and water evolution ($m/z = 18$) due to the reduction show two distinct maxima. The intermediate stage of reduction is also observed on the TG curve. The corresponding DTG curve (not shown) exhibited two maxima at temperatures 535 and 632°C, which is in agreement with the TPR data obtained with the same heating rate (10 K min^{-1}) and hydrogen concentration (6 vol%) in the carrier gas. The weight-loos on the TG curve, 1.35%, indicates a vanadia content of 7.67 wt% which agrees with the content determined by TPR and confirmed by other analytical methods, such as atomic absorption, volumetric or potentiometric redox titration and XRF [10].

C) Organic residues in sol-gel derived catalysts

Thermal analysis can be applied not only for determining the active components in multiphase catalytic materials, but also for measuring undesired impurities present in catalysts after synthesis. The application of TA is illustrated using as an ex-
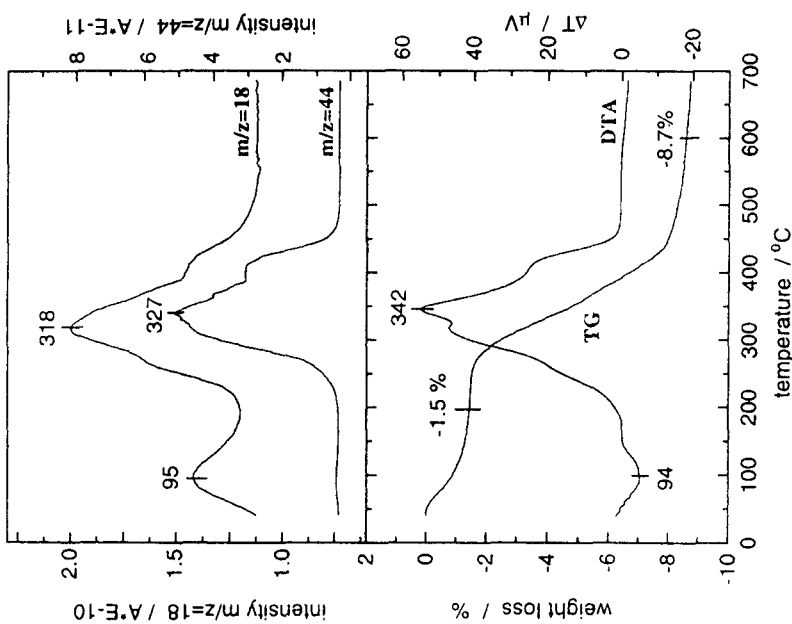
Fig. 8 Calcination of zirconia-aerogel in air studied by TA-MS

Fig. 7 Reduction of V_2O_5 in titania-supported vanadia catalyst by 6 vol% hydrogen in argon, studied by TA-MS

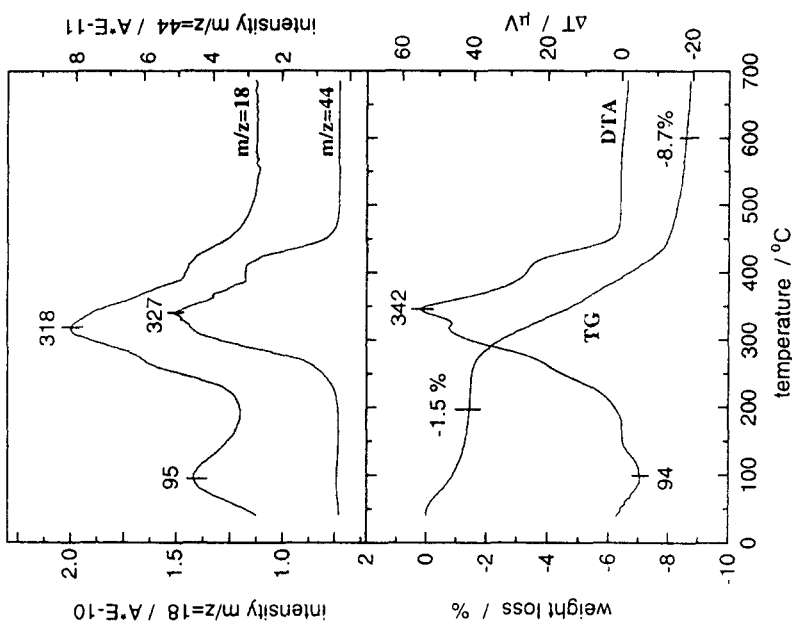ample the determination of the amount of organic residues in catalysts, such as zirconia and mixed titania-silica prepared by the sol-gel method.

Zirconia is widely used as catalyst or catalyst support. Its catalytic behaviour originates from both, acid-base and redox properties. Among the different preparation methods applied [13] the combination of the solution-sol-gel technique with supercritical drying offers the advantage of producing zirconia aerogels with high surface areas in the range of 200–400 $m^2 g^{-1}$. Aerogels with meso- to macroporosity were prepared by an acid-catalyzed alkoxide-sol-gel route with tetrabutoxyzirconium(IV) and subsequent high-temperature supercritical drying at 305°C [14]. The effect of solvent, calcination temperature and drying method (conventional drying leads to the formation of xerogels, supercritical drying to aerogels) was studied by thermal analysis among other methods.

Characteristic features of an uncalcined zirconia-aerogel, as revealed by TA-MS, are shown in Fig. 8. The observed weight loss originates mainly from the evolution of water (desorption of physisorbed water, dehydroxylation) and oxidation of organic residues present in the aerogel. These conclusions can be drawn from relating the TG and DTA curves to the recorded ion intensities of $m/z=44$ (CO_2) and $m/z=18$ (H_2O). The evolution of water begins at ambient temperature and reaches maxima at 95 and 318°C, respectively. The first water liberation stems primarily from physisorbed water (small endo-peak of DTA curve). At higher temperature the evolution of adsorbed water is superimposed by the formation of water due to the oxidation of organic contaminants, as indicated by the exothermic effect on the DTA curve and the accompanying formation of CO_2. With increasing calcination temperature, the amount of organic residues decreases. The carbon content of the uncalcined zirconia aerogel, determined from the amount of evolved CO_2 after calibration of the mass spectrometric curve [15], was ca. 5 wt%, as confirmed by elemental microanalysis. For the samples calcined in air at 300 and 500°C, the amount of carbon decreased to ca. 0.9 and 0.3 wt%, respectively. The higher amount of organic residues in xerogels seems to be responsible for the significantly lower surface density of acid sites on these materials compared to corresponding aerogels, leading to a marked difference in the catalytic behaviour.

The potential of TA for the determination of carbon impurities can also be illustrated using the example of mesoporous titania-silica aerogels with highly dispersed titanium [16]. These catalysts, which show excellent activity in the epoxidation of bulky olefins [17], are prepared via an alkoxide-sol-gel process with subsequent semi-continuous extraction using supercritical CO_2. Thermoanalytical investigations of uncalcined titania-silica aerogels indicated, as in the case of the aforementioned zirconia aerogels, the presence of significant amounts of carbon. A comparison of the TA curves with the MS results led to the conclusion that the higher carbon content of low-temperature (ca. 30°C) dried aerogels is due to residual alcohol (solvent), trapped in the porous network, whereas with high-temperature (ca. 230°C) dried aerogels the presence of carbon is mainly attributed to the realkoxylation of surface hydroxyl groups during supercritical drying [18].
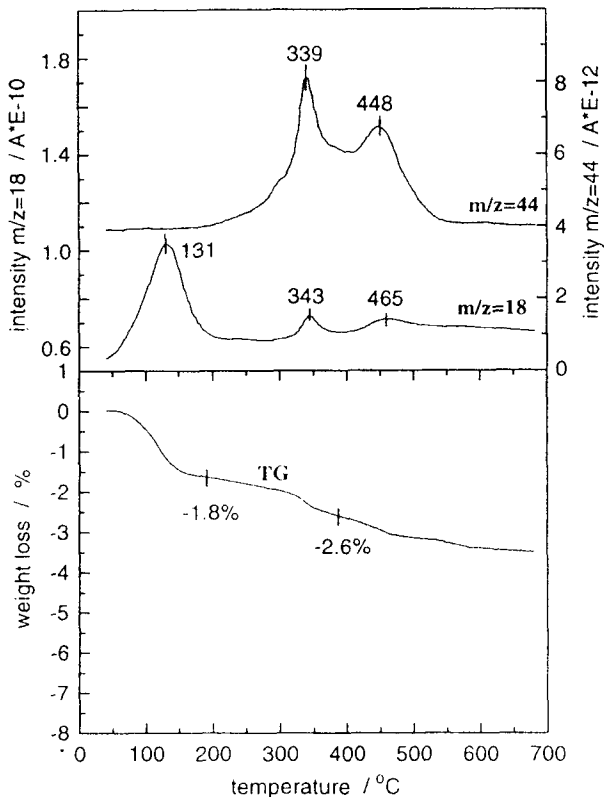
Fig. 9 Determination (TA-MS) of carbon content of titania-silica aerogel previously calcined in air at 600°C

The amount of carbon could only be reduced below 0.2–0.3 wt% when samples were calcined at temperatures up to ca. 600°C. The determination of these small amounts of carbon is illustrated in Fig. 9. CO_2 evolution, revealed by two distinct peaks on the mass spectrometric curve $m/z = 44$, indicates the presence of traces (0.25 wt% of carbon) of organic residues in the calcined aerogel. This result, confirmed by elemental analysis, demonstrates the sensitivity of TA-MS measurements and proves that such small amounts of components can be determined.

Further examples of the application of TA-MS in catalyst characterization, such as the identification of the active phase in supported CrO_x/TiO_2 catalysts [19, 20], or the determination of the phase composition of a potassium-promoted iron oxide catalyst during the dehydrogenation of iminodibenzyl [21], have been reported in the literature. In the case of supported chromia/titania catalysts, thermal analysis revealed several so far unknown details of the complex reactions occurring during catalyst preparation.

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