Chapter 2
Thermal Analysis and Calorimetry Techniques for Catalytic Investigations

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Abstract   The use of thermal analysis and calorimetry techniques is quite an old and known field of applications for the catalytic investigations and many publications have been published on the various topics including analysis of catalysts, investigation of the processes during the preparation of catalysts, desactivation of catalysts and interaction of reactants or catalytic poisons with the catalysts. Differential thermal analysis, calorimetry and thermogravimetry are also used to characterize the catalysts, especially in the field of gas–solid and gas–liquid interactions. Since the last years, many technical improvements have appeared in the design and the use of thermal analyzers and calorimeters, particularly for the characterization of catalysts. This chapter gives a detailed overview of the uptodate thermal techniques covering various techniques including Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC), the calorimetric techniques (including Isothermal Calorimetry, Titration Calorimetry), Thermogravimetric Analysis (TGA), the combined techniques (including TG-DTA and TG-DSC), the Evolved Gas Analysis (including TG-MS, TG-FTIR). Some examples of applications are given to illustrate the catalyst characterizations.

2.1 Introduction

The use of thermal analysis and calorimetry techniques is quite an old and known field of applications for the catalytic investigations and many publications have been published on the various topics. In 1977, Habersberger [19] has published a short review of the possibilities of applications of thermal analysis to the investigation of catalysts including analysis of catalysts, investigation of the processes during the preparation of catalysts, desactivation of catalysts and interaction of reactants

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or catalytic poisons with the catalysts. In 1994, Auroux [4, 8] has described the different thermal techniques including differential thermal analysis, calorimetry and thermogravimetry that are used to characterize the catalysts, especially in the field of gas–solid and gas–liquid interactions. More recently in 2003, Pawelec and Fierro [45] have prepared a chapter called "Applications of thermal analysis in the preparation of catalysts and in catalysis" for the "Handbook of Thermal Analysis and Calorimetry". Since the last years, many technical improvements have appeared in the design and the use of thermal analyzers and calorimeters, particularly for the characterization of catalysts. Following the summer school of calorimetry named "Calorimetry and thermal methods in catalysis" organized in Lyon (France) since 2007, this chapter will give a detailed overview of the uptodate thermal techniques presented during this meeting with some examples of applications for catalyst characterization.

2.2 Thermal Analysis and Calorimetry: Techniques and Applications

Thermal Analysis (TA) means the analysis of a change in a sample property which is related to an imposed temperature alteration and calorimetry means the measurement of heat [24]. The corresponding property of the sample is measured according to time and temperature with the main following techniques:

- Temperature difference >>> Differential Thermal Analysis (DTA).
- Heat flux variation >>> Differential Scanning Calorimeter (DSC).
- Heat variation >>> Calorimetry.
- Mass change >>> Thermogravimetry (TG).
- Length or volume change >>> Thermomechanical Analysis (TMA).

There is no one method of measurement in thermal analysis and calorimetry that can be used for all materials or to cover all the possible thermal properties and applications. A measurement method has to be selected depending on the following criteria:

- the parameter to be measured (temperature, heat, mass or length),
- sample type (solid or liquid),
- sample size,
- sample reactivity (which affects choice of crucible, protective gas),
- range of temperature,
- atmosphere around the sample (inert, oxidative, reducing),
- operation under pressure,
- operation in a corrosive gas,
- operation in humid atmosphere,
- sensitivity of detection in changes of mass, heat and length,
- whether a combined technique is necessary, . . .

According to the different thermal techniques and the selection of the experimental parameters, a large selection of applications is available for the characterization of catalysts and related materials, and also the simulation of the catalytic processes. The Table 2.1 provides a brief overview of the main applications that have been developed.

2.3 The Differential Thermal Analysis Technique

2.3.1 Principle

ICTAC (International Confederation for Thermal Analysis and Calorimetry) gives the following definition for the DTA technique: "A technique where the temperature difference between a sample and a reference material is measured while they are subjected to the same temperature variation (heated or cooled) in a controlled atmosphere" [25]

The Differential Thermal Analysis technique is based on a differential mounting of thermocouples in the sample (S) crucible and reference (R) crucible (Fig. 2.1). The device is located in a block heated (or cooled) at a controlled temperature.

The electric signal (emf) measured at the ends of the thermocouple is proportional to the difference of temperature, ΔT, between the sample and reference sides.

The temperature of the furnace (T_p) is programmed with a linear heating rate (Fig. 2.2). The reference temperature (T_r), measured in an inert material (that means a material that does not undergo a thermal transition for the given temperature range

Table 2.1 Techniques and applications in thermal analysis

| Physical property	Technique	Application
Temperature	Differential thermal analysis (DTA)	Phase change, dehydration, desorption, decomposition, reduction, oxidation, ...
Heat flow	Differential scanning calorimetry (DSC)	Phase change, adsorption, absorption, hydrogenation, dehydration, desorption, decomposition, dehydrogenation, reduction, oxidation, catalysis, heat capacity, kinetics, ...
Heat	Calorimetry	Reaction, adsorption, absorption, hydration, mixing, formation, catalysis, thermodynamics, heat capacity, kinetics, ...
Mass	Thermogravimetric analysis (TGA)	Adsorption, hydrogenation, dehydration, desorption, decomposition, dehydrogenation, oxidation, kinetics, ...
Length, volume	Thermomechanical analysis (TMA)	Phase change, expansion, sintering, ...
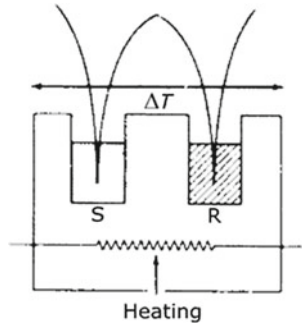
Fig. 2.1 DTA principle
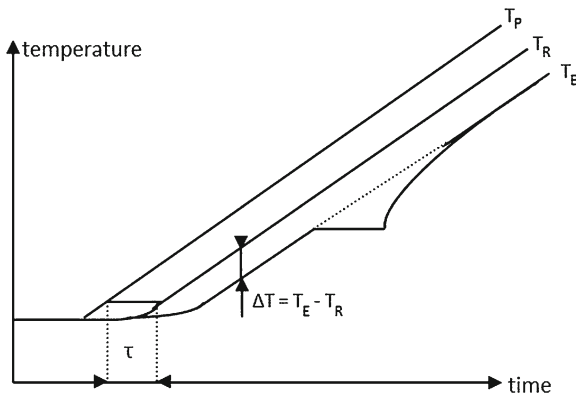
Fig. 2.2 DTA principle—recording of the different temperatures

of investigation) follows this heating profile with a small delay due to the thermal gradient in the crucible.

The sample temperature (T_e), measured in the sample material under investigation, follows in the same way the heating profile until a thermal transition in the sample is reached. In the case of melting, the temperature of the sample remains constant during melting (this is the melting plateau). When melting is complete the sample temperature changes to then follow the heating profile.

By measuring the difference between the sample temperature and the reference temperature, the thermogram (Fig. 2.3) is obtained, describing the melting peak.

From this curve, a first information is obtained: the temperature of melting of the material. In a case of a pure sample, this temperature corresponds to the onset temperature of the melting peak.

Attention: Such a principle described on Fig. 2.1 does not experimentally exist. In fact there is a risk of interaction between the thermocouple and the material that will affect the measure. In the experimental DTA device, a crucible has to be used as an interface between the thermocouple and the sample.
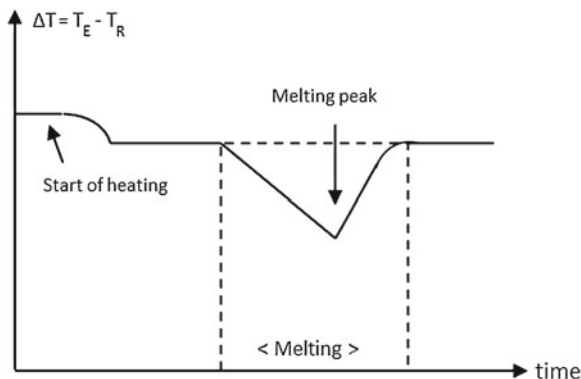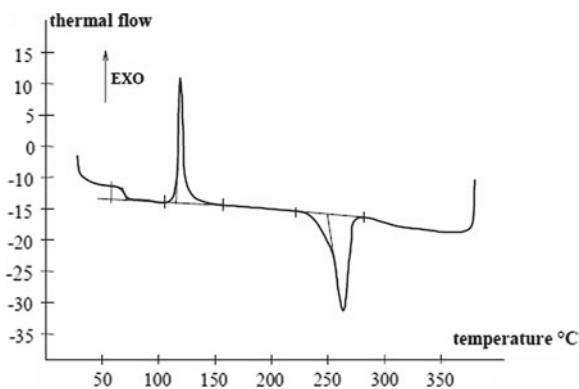
Fig. 2.3 Melting thermogram

Fig. 2.4 The DTA thermogram

The DTA technique also gives another important information on the type of transition, either endothermic or exothermic effect. The endothermic tranformation produces a decrease of the temperature that means that ΔT is negative. For an exothermic transformation, a positive ΔT is recorded. The DTA thermogram (Fig. 2.4) allows making a clear identification of the different types of transformations according to the side of the peaks.

Among the different types of endothermic and exothermic effects, the following list can be given when catalysts are under investigation:

- Endothermic: melting, evaporation, sublimation, dehydration, dehydroxylation, desorption, and pyrolysis.
- Exothermic: crystallization, adsorption, oxidation, combustion, hydrogenation, and decomposition.

A variation of the base line may also be detected on the DTA curve (the first transition on Fig. 2.4). This is the signature of a glass transition, expressing that the material contains an amorphous phase.

2.3.2 Detectors

A standard DTA detector is shown in Fig. 2.5. Two different types of metals are used to build the DTA arrangement. Different types of thermocouples are used to produce DTA detectors according to the range of temperature to be investigated (Table 2.2). The sensitivity of the detector varies with the nature of the thermocouple. Higher sensitivity is obtained with types of thermocouples in the top part of Table 2.2.

A crucible is adjusted on each side of the DTA rod for the sample and the inert material. The crucible volume varies from 20 to 100 µl.

The choice of the crucible is a very important step in the DTA experimentation. It is needed that there is no interaction between the crucible and the sample during the test. In the same time it is needed that the crucible is a good heat conductor in order
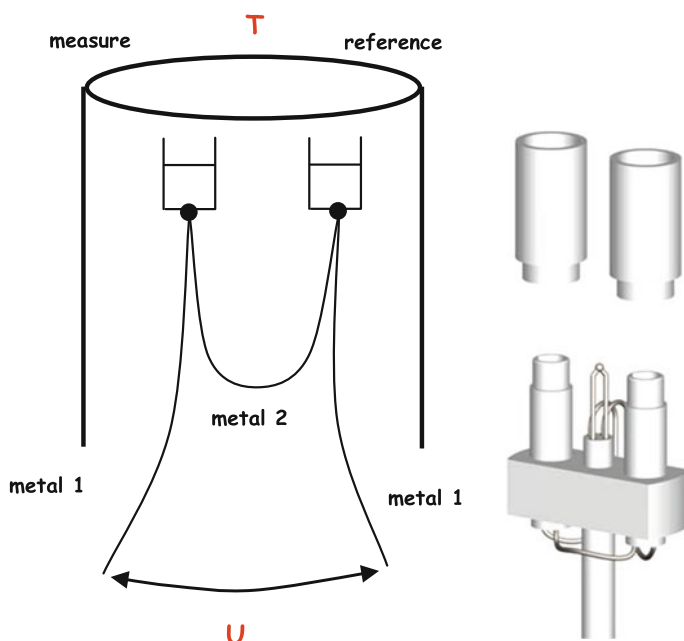

Fig. 2.5 Principle and cross section of a DTA detector

Table 2.2 Different types of thermocouples used for DTA detectors

Type	Composition	Temperature range
Platinel	55Pd 31Pt 14Au/65Au 35Pd	$-150\,°C \rightarrow 1000\,°C$
E	Ni Cr/Cu Ni = Chromel/Constantan	$-50\,°C \rightarrow 800\,°C$ ($500\,°C$ under air)
S	Pt Rh10 %/Pt	$1600\,°C$ ($1000\,°C$ under H_2)
B	Pt Rh30 %/Pt Rh6 %	$1750\,°C$ ($1000\,°C$ under H_2)
W5	W Re26 %/W Re5 %	$2400\,°C$/inert atmosphere

to ensure a good heat transfer between the sample and the thermocouple. Different materials are used to produce adequate crucibles:

- Aluminium (up to 500 °C),
- Alumina (especially required for metallic samples),
- Platinum (especially required for inorganic samples),
- Graphite and tungsten (for temperature above 1750 °C).

According to experimentation and corrosion problems, other types of materials are available such as magnesia, zirconia, boron nitride, . . .

2.3.3 Operation

In most experimentations, the DTA crucible is used open. A cover is needed especially in the two following situations:

- The vapour has to be retained above the sample, in the case of dehydration or decomposition. For such an experiment a cover with a pin hole is used.
- There is a risk of overflowing of the sample when decomposing. In such a case it is recommended to close the crucible with a lid to avoid the destruction of the DTA rod.

As the crucible is open, the control of the gas above the sample is a very important parameter. Different types of gas atmosphere are available according to the experiment to be run:

- Inert atmosphere (nitrogen, argon, helium) to protect the sample from any oxidation.
- Oxidative atmosphere (air, oxygen) to be used for oxidation and combustion investigations.
- Reactive gas (hydrogen, carbon monoxide, ammonia, . . .) for adsorption and absorption reactions.
- Water vapour for hydration reactions.

2.3.4 Applications

The applications of the DTA technique are quite wide for the characterization of the catalysts and related products, but they are mainly oriented on the determination of their structural properties. Here below is a non exhaustive list of DTA applications:

- Melting and crystallization,
- Phase transitions (glass transition, order–disorder, . . .),
- Preparation of catalyst: dehydration and dehydroxylation,
- Rapid screening of potential catalysts,
- Evaluation of the effects of various pretreatments,

- Adsorption, desorption,
- Decomposition,
- Oxydation, reduction,
- Regeneration of catalyst, . . .

The DTA applications applied to catalysts and more generally to inorganic materials have been extensively reviewed in various books [23, 33, 44, 45, 48, 61].

2.4 The Differential Scanning Calorimetry Technique

2.4.1 Principle

Differential Scanning Calorimetry is defined as followed by ICTAC:
"A technique in which the heat flux (thermal power) to (or from) a sample is measured versus time or temperature while the temperature of the sample is programmed, in a controlled atmosphere. The difference of heat flux between a crucible containing the sample and a reference crucible (empty or not) is measured." [25].

In a heat flux DSC, the specimen surroundings (generally the furnace and detector) are at constant temperature (isothermal mode) or at a variable temperature (scanning temperature mode). A defined exchange of heat takes place between the specimen and its surroundings (Fig. 2.6). The amount of heat flux (heat flow rate) is determined

Fig. 2.6 Heat flux DSC principle
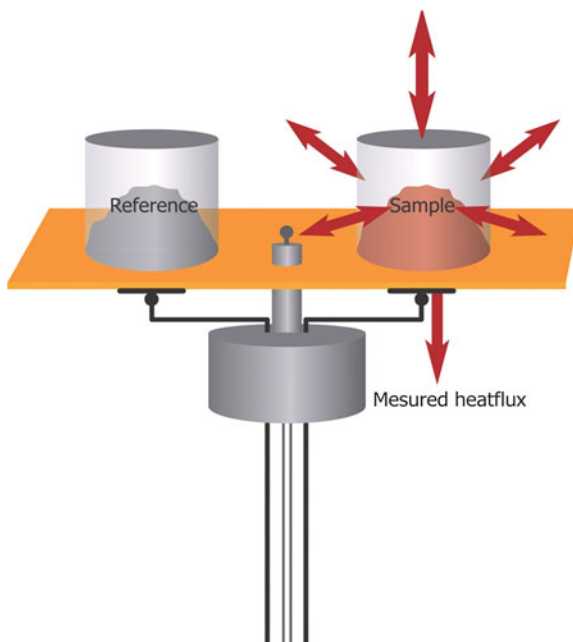
on the basis of the temperature difference along a thermal resistance between the specimen and its surroundings.

The heat flux for a given sample at a temperature T_s is equivalent to:

$$dq_s/dt = -dh/dt + C_s dT_s/dt \quad (2.1)$$

where:

- dh/dt: Heat flux produced by the transformation of the sample or the reaction.
- C_s: Heat capacity of the sample, including the container.

The heat flux dq_s/dt is exchanged with the thermostatic block at a temperature T_p through a thermal resistance R according to the following relation;

$$dq_s/dt = (T_p - T_s)/R. \quad (2.2)$$

From the relation (2.1), it is seen that the thermal contribution due to the heat capacity of the sample and container is significant and will provide a major disturbance at the introduction of the container in the calorimeter. From the relation (2.2), it is also evident that any temperature perturbation of the thermostatic block will affect the calorimetric measurement.

In order to solve these different problems, a symmetrical design is used. An identical crucible with an inert material (the reference container can also be empty) is placed on the detector at the same T_p temperature.

The difference of heat flux is measured between the two sides:

$$dq/dt = dq_s/dt - dq_r/dt = -dh/dt + C_s dT_s/dt - C_r dT_r/dt \quad (2.3)$$

where:

- C_r: Heat capacity of the reference, including the container.
- T_r: Temperature of the reference.

The relation (2.2) becomes:

$$dq/dt = (T_r - T_s)/R$$

or by derivation

$$Rd^2q/dt^2 = dT_r/dt - dT_s/dt \quad (2.4)$$

By combination of relations (2.3) and (2.4), the characteristic equation for the calorimetric measurement is obtained:

$$dh/dt = -dq/dt + (C_s - C_r)dT_p/dt - RC_s d^2q/dt^2. \quad (2.5)$$

If dh/dt corresponds to an absorbed thermal power due to an endothermic transformation or reaction, the dh/dt value is positive.

If dh/dt corresponds to a released thermal power due to an exothermic transformation or reaction, the dh/dt value is negative.

dh/dt (heat flow rate) is related to the kinetics of the transformation. The shape of the DSC peak gives a first indication on the rate of reaction.

When dh/dt is null (no transformation), the Eq. (2.5) allows to access the heat capacity of the sample. DSC provides a direct and accurate measurement of the specific heat of any type of material.

If the DSC test is run isothermally, the parameter dT_p/dt is null. In the case of a small perturbation of the temperature T_p of the thermostatic block, the corresponding thermal effect will be minimized if the C_s and C_r heat capacities are similar.

The last term $R\,C_s d^2 q/dt^2$ (called also thermal lag) that affects the measurement mostly depends on the thermal resistance or also the time of response of the DSC on one side, and the heat capacity of the sample and container on the other side. For long period of time ($t >> RC_s$) it will be negligible.

As seen before with DTA (Fig. 2.4), the DSC curve will show endothermic and/or exothermic effects according to the transformations and the reactions.

If DTA is more considered as a qualitative technique, the sophisticated DSC detectors define a quantitative and accurate determination of the heat effects.

From the DSC curve different important information are obtained (Fig. 2.7):

- the temperature of the transformation (generally measured at the top of the peak),
- the heat related to the transformation, and
- the rate of the transformation.

In order to get accurate measurements of temperature of transition, the DSC has to be calibrated using reference materials [20]. The experimental procedures for such a correction are described in different standards, especially ISO standard [26].

As the DSC signal is equivalent to a thermal power (expressed in mW), the integration of the DSC peak between the time t_i (start of the peak) and t_f (end of the
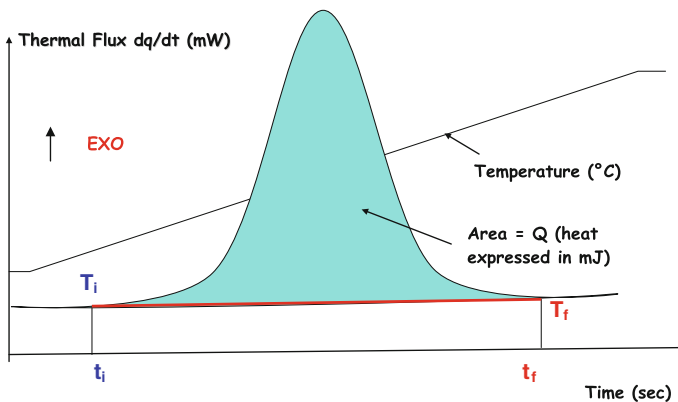

Fig. 2.7 DSC curve

peak) corresponds to the area under the peak, delimited by the line drawn between the two points.

Before getting the corresponding heat value, a calibration of the DSC detector is also needed. The raw DSC signal is an electrical signal provided by the thermocouples, expressed in microvolt. To convert this signal in microwatt, the use of reference materials with known heat of melting is required [20].

However another calibration technique is available when the Calvet type DSC is used. The principle is to apply a known amount of power in a dedicated calibration vessel. To reach this target, a resistance is embedded in the crucible. A known current I is delivered and the corresponding tension U measured, providing the power $P = UI$ that is applied. The corresponding Joule effect provides a DSC exothermic deviation in microvolt (Fig. 2.8). Such an electrical calibration is very interesting as it can apply at any temperature, even at constant temperature. This will be more detailed in paragraph 5 for the calorimetric techniques.

The other important information associated to the DSC peak is related to the kinetics of the transformation. As the DSC signal corresponds to a heat flow rate, the shape of the peak directly informs on the rate of the transformation. For example a sharp peak indicates a high rate of reaction. At the top of the peak, dh/dt_{max} (Fig. 2.7), the rate of the reaction reaches the maximum value. This information will be used in many models for the determination of the kinetic parameters of a transformation.

2.4.2 Detectors

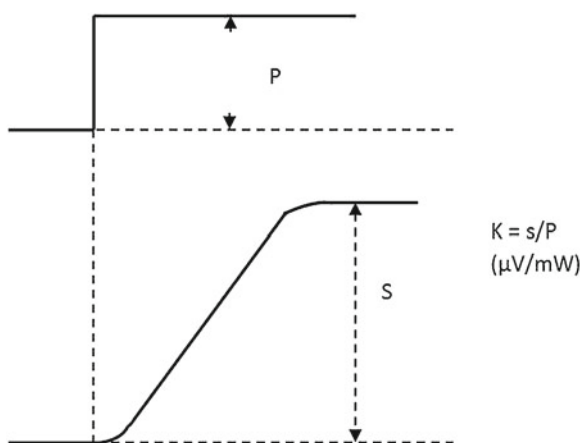Different types of DSC techniques are available and are described in Table 2.3.

Fig. 2.8 Principle of the DSC electrical calibration using the Joule effect

Table 2.3 Different types of DSC techniques

Property	Technique	Description
Heat flow rate	Heat flux DSC	A technique in which the difference in heat flow rate to a test sample and to a reference sample is analysed while they are subjected to the same temperature variation (heated or cooled). The detector is a plate-DSC detector.
Heat flow rate	Power compensated DSC	A technique in which the temperature difference between a test specimen and a reference specimen occurring through subjecting both specimens to the same controlled temperature program is compensated by appropriately adjusting the difference of heating power to the test and reference specimen. The differential heating power is recorded against temperature or time.
Heat flow rate	Calvet DSC	A technique in which the difference of heat flow rate to the sample and to the reference sample is analysed while they are subjected to a temperature variation (heated or cooled). The detector is a cylindrical DSC detector.
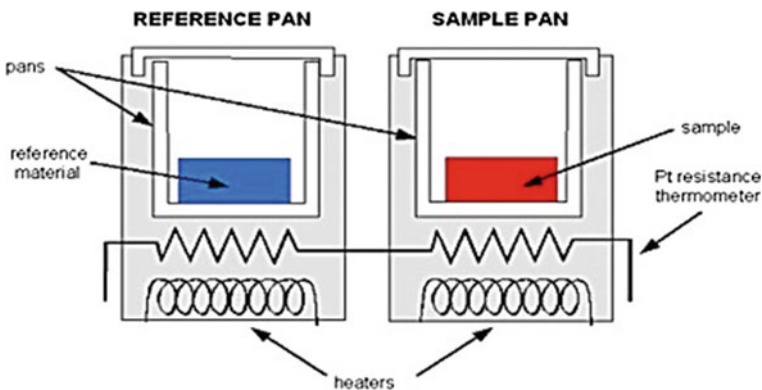
Fig. 2.9 DSC power compensation principle

For the heat flux plate DSC (Fig. 2.6) and the power compensation DSC (Fig. 2.9), the common characteristic is that they both use a flat-shaped sensor.

The principle of the power compensated DSC [37] is different from the heat flux DSC described previously. The heaters beneath the pans aim to minimise the difference in temperature between a specimen and an inert material. When a transition occurs in the specimen, the reference heater will aim to compensate for this and keep the reference pan at a similar temperature. Individual platinum resistance thermometers measure the temperature of each pan, and the power required to maintain this

state is recorded. Endothermic and exothermic transitions are recorded depending if power is added or subtracted.

Even if the measurement principles are quite different, the heat transfer from (or to) the sample is about the same. The sample, contained in a metallic crucible, is placed and centered on the plate acting as a flat-shaped sensor. A reference crucible (empty or containing an inert material) is placed on the other plate.

The basics of the plate DSC is that the heat exchange between the sample and the detector is done through the bottom of the crucible, corresponding to a two dimensional detection. In fact only a part of this heat transfer is measured, as a significant part is dissipated through the walls and the cover of the crucible (Fig. 2.6). If the efficiency ratio is considered, that means the heat flux measured by the sensor to the total heat flux produced by the thermal event, a simulation using a thermal modeling software shows that only around half of the heat flux is dissipated through the plate [13, 31]. The Fig. 2.10 clearly shows that the efficiency rapidly decreases with the temperature and the thickness for the plate. The efficiency is also affected by the amount of the sample under investigation. This is why it is recommended to work with small amounts of material (about 5–10 mg) when using a plate DSC, in order to minimize the heat losses. The thermal conductivities of the crucible and the gas used in the experimental chambers also are very important parameters to be considered in the efficiency of the heat exchange. For example a very heat conductive gas (helium) will favour the heat transfer between the crucible and the detector, but in the same time increase the heat losses. So the calibration of a plate-type DSC is very critical and has to be run with the experimental conditions that are selected for the sample test. The Calvet type DSC offers another technical option [38].

The detection concept is based on a three dimensional fluxmeter sensor. The fluxmeter element consists in a ring of several thermocouples in series (Fig. 2.11). The corresponding thermopile of high thermal conductivity surrounds the experimental space within the calorimetric block. The radial arrangement of the thermopiles guarantees an almost complete integration of the heat. This is verified by the calculation of the efficiency ratio that indicates that an average value of $94 \pm 1 \%$ of heat is transmitted through the sensor on the full range of temperature of the Calvet type DSC (Fig. 2.12). Another very important point is that the sensitivity of the DSC is no more affected by the type of crucible, the type of purge gas and flow rate.

Fig. 2.10 Efficiency ratio of a flat-shaped DSC as a function of the sensor plate thickness
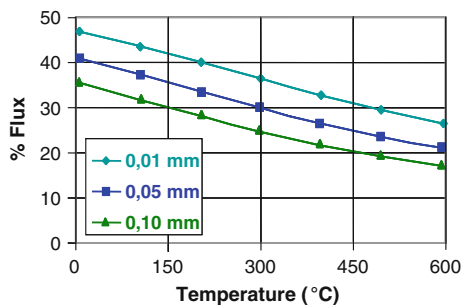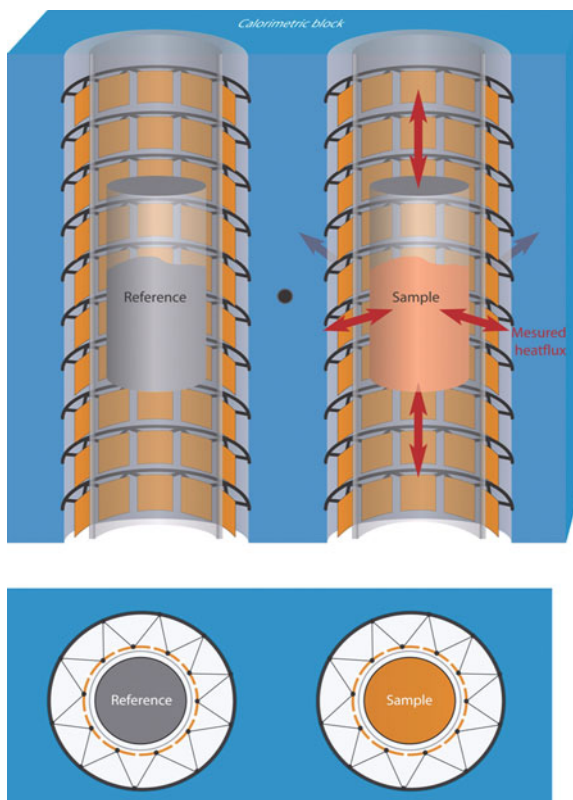
Fig. 2.11 Schematic of the Calvet principle

One of the main advantages of the Calvet-type DSC is that larger amounts of sample can be investigated. The open tube detection allows the adaptation of different types of experimental crucibles, especially with the possibility of introduction of various types of gas under normal or high pressure. This design specificity is of a great interest for the applications on catalysts, and more generally for all the adsorption investigations.

2.4.3 Operation

The selection of the crucible for the sample is one of the most important task to get a good experiment. The choice depends on a series of parameters that has to be very clearly identified:

- The nature of the crucible: various materials are available (aluminium, platinum, gold, stainless steel, . . .) according to the temperature range. It is important that no interaction occurs between the sample and the crucible during the test.
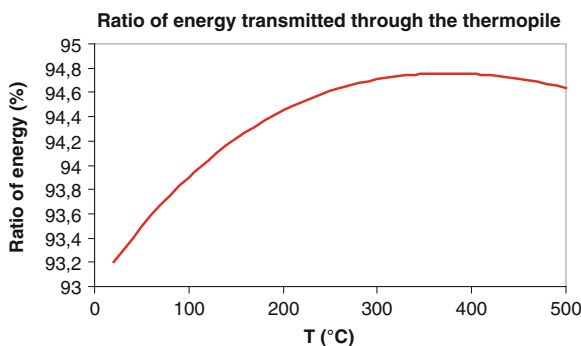
Fig. 2.12 Efficiency ratio of a Calvet type calorimeter versus temperature

- The way of using the crucible:
  - closed with a lid: this is the most common use for a DSC crucible. It is very convenient for any type of transition or transformation as soon as the vapour pressure of the sample remains low during the test
  - closed with a pierced lid: the hole is to favour the escape of vapour from the crucible, for example during a dehydration
  - open: this situation is needed when a gas interaction with the sample is investigated, for example an adsorption
  - tightly closed: dedicated crucibles are available to keep the vapour inside the crucible during a reaction. As this will produce an increase of the vapour pressure, a tight closing of the crucible is strictly needed.

Two other types of crucibles, that can be only used with a Calvet type DSC are also described as they find specific applications for catalytic investigations.

The first type of crucible is a quartz reactor that is designed for the investigation of gas adsorption on powders (Fig. 2.13).

The quartz tube is introduced in the Calvet type DSC (set in the vertical position). A fritted glass substrate is located in the middle of the tube to receive the powdered sample in order to be surrounded by the calorimetric detector. Tight connections are adjusted at both ends of the tubes for the gas inlet and outlet.

By using a gas injection loop, pulses of known volume of reactive gas are introduced on the sample [4, 9, 16, 46, 50]. The DSC signal gives the corresponding heat of adsorption. In order to know if the total volume of gas is adsorbed on the sample, a GC detector is set on-line with the DSC. The outlet gas is analyzed and the corresponding amount of non adsorbed gas measured.

This DSC-GC coupling allows correlating the heat of adsorption to the amount of gas adsorbed on the sample.

The use of a quartz tube makes also possible to use any type of gas (even corrosive gas) for such an investigation.
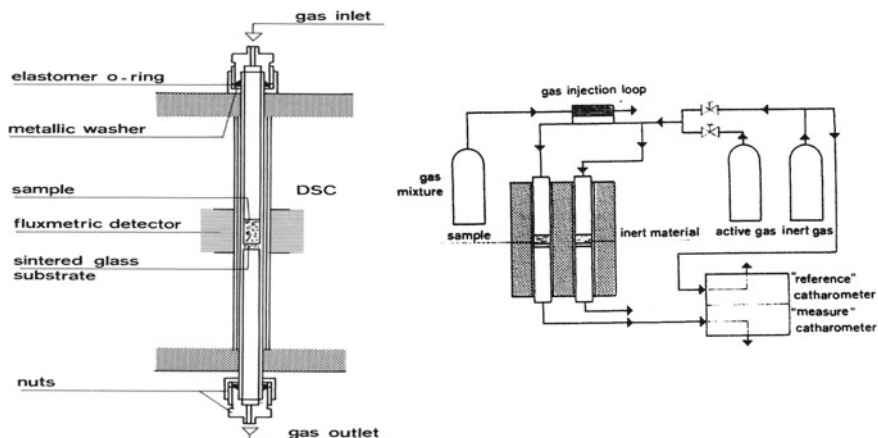
Fig. 2.13 Quartz reactor for adsorption studies and coupling with the gas introduction and analysis device
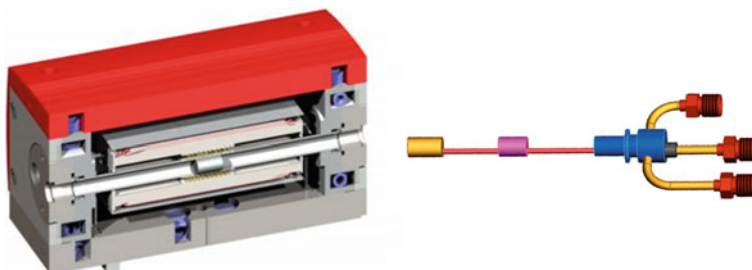

Fig. 2.14 Controlled high pressure crucible with the Calvet type DSC

The second interesting type of crucible is dedicated to work under a controlled gas pressure. Today more and more works are done on the adsorption of hydrogen to form metal hydrides used for the storage of hydrogen. Such investigations have to be run under a controlled pressure of hydrogen and a given temperature, or range of temperature.

After introducing the sample, the crucible (made of incoloy) is tightly closed with a screwable stopper, then introduced in the tube of the Calvet type DSC (Fig. 2.14). A pressure of gas is applied through an external high pressure panel.

Using such an experimental design, only the small volume containing the sample is under pressure. The DSC detector itself remains under normal pressure.

This is very convenient for safety reasons especially when hydrogen is used, but also for the DSC calibration as it is not affected by the gas pressure. A current pressure of 400 bar is available on such a vessel up to 600 °C.

Two different modes are used for the investigation of absorption and decomposition of metal hydrides:

- Operation in temperature scanning mode with a constant gas pressure.
- Operation at constant temperature with a variable pressure.

2.4.4 Applications

The DSC applications for catalytic investigations are very similar to the ones described previously for the DTA technique. However the DSC measurement gives more possibilities as described in Sect. 4.3, especially for adsorption investigations under normal [57] or high pressure [51]

The DSC technique also offers more flexibility for coupling with other techniques (thermogravimetry, gas analysis).

DSC can also be used for the Thermal Programmed Desorption (TPD) determination coupled with a gas analyzer [11, 34]

Among the applications that are specific to the DSC technique, the determination of heat capacity is one of the most important. Different methods can apply for this measurement and are described below.

2.4.4.1 Heat Capacity Determination

Heat capacity plays an important role in thermal processes in any type of industry. Heat loads and processing times, and industrial equipment sizes are influenced by the heat capacity of the material. Combined with thermal conductivity and thermal diffusivity, heat capacity data are needed for the modelisation of the thermal processes. Heat capacity varies with temperature, composition and also water content. As the material can be under the solid or the liquid form, different ways of measuring heat capacity using the calorimetric techniques have been developed.

Heat capacity is thermodynamically defined as the ratio of a small amount of heat δQ added to the substance, to the corresponding small increase in its temperature dT:

$$C = \delta Q/dT$$

For processes at constant pressure, the heat capacity is expressed as:

$$C_p = (\delta H/\delta T)_p$$

Though DSC is a very well adapted technique to measure heat capacity [52], only one procedure has been essentially developed using a continuous heating mode for solid samples. In this chapter, another procedure is described using a step heating mode.

c_p Determination in the Temperature Scanning Mode

If there is no transformation for the considered temperature range, the calorimetric signal for a given mass of sample heated at a constant heating rate dT/dt is relative to the following relation for the sample side:

$$(dq/dt)_s = (m_s c_{p(s)} + m_{cs} c_{p(cs)})dT/dt \qquad (2.6)$$

where:

- m_s and m_{cs} respectively sample mass and vessel mass (including the cover),
- $c_{p(s)}$ and $c_{p(cs)}$ respectively specific heat capacity of sample and its vessel.

On the reference side, an empty vessel is used giving the corresponding signal:

$$(dq/dt)_r = m_{cr} c_{p(cr)} dT/dt \qquad (2.7)$$

where:

- m_{cr} respectively reference vessel mass,
- $c_{p(cr)}$ respectively specific heat capacity of reference vessel (equal to $c_{p(cs)}$ as the nature of the vessel is identical).

The differential calorimetric signal is given by the following relation:

$$(dq/dt)_s = (m_s c_{p(s)} + m_{cs} c_{p(cs)} - m_{cr} c_{p(cr)})dT/dt \qquad (2.8)$$

In order to get rid of the thermal effect of both vessels, the same test (called blank test) is run with identical empty containers. From a practical point of view, the reference vessel is not removed from the calorimeter. The corresponding relation is obtained:

$$(dq/dt)_b = (m_{cs} c_{p(cs)} - m_{cr} c_{p(cr)})dT/dt \qquad (2.9)$$

By subtracting the two calorimetric traces, the specific heat capacity of the sample is extracted (Fig. 2.15):

$$C_{p(s)} = (1/m_s)[(dq/dt)_s - (dq/dt)_b]/dT/dt. \qquad (2.10)$$

As seen before in the calibration paragraph, the calibration using the Joule effect technique allows converting any calorimetric signal in mW without the need of standard reference materials. That means that in relation (2.10) all the parameters (sample mass, calorimetric signals, heating rate) are accurately known to determine the specific heat capacity of the sample $C_{p(s)}$ (expressed in $J.g^{-1}.°C^{-1}$) at a given temperature. The variation of $C_{p(s)}$ versus temperature can be determined.
With the DSC technique, a third test is needed using a standard reference material (sapphire) that has a known specific heat capacity.

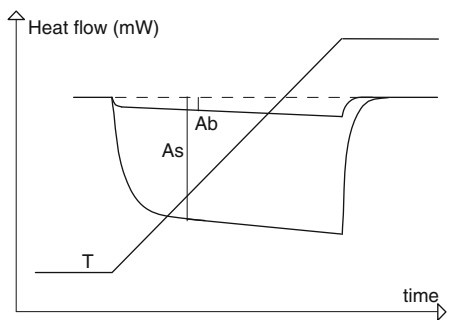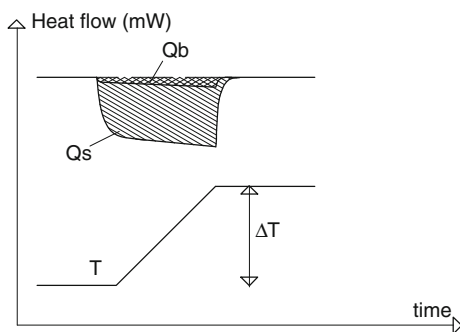**Fig. 2.15** c_p determination in the temperature scanning mode

Fig. 2.16 c_p determination in the step heating mode

c_p Determination in the Temperature Step Mode

The previous described technique is very easy to use, but shows some drawback as soon as the accuracy of the c_p determination is concerned. With the temperature scanning mode, the sample is continuously heated and is never at the thermal equilibrium. However c_p is a thermodynamical parameter, defined at the thermal equilibrium. The temperature step mode has been developed to answer this limitation. A step of temperature is applied to the sample and the thermal equilibrium (characterized by the signal return to the baseline) is waited after each step (Fig. 2.16).

If the relation (2.8) is integrated between time t_o (beginning of the step) and time t_n (return to the baseline):

$$\int (dq/dt)_s dt = \int [(m_s c_{p(s)} + m_{cs} c_{p(cs)} - m_{cr} c_{p(cr)}) dT/dt] dt. \qquad (2.11)$$

the corresponding equation is obtained:

$$[Q]_{to}^{tn} = (m_s \bar{c}_{p(s)} + m_{cs} \bar{c}_{p(cs)} - m_{cr} \bar{c}_{p(cr)}) \Delta T \qquad (2.12)$$

where $\bar{c}_p$ corresponds to the mean c_p value between the two temperatures defining the step of temperature.

Q is obtained by integrating the corresponding surface defined by the calorimetric signal between t_o and t_n.

If again the signal corresponding to the blank test is subtracted when an identical step of temperature is applied, the final relation giving the mean c_p of the sample is obtained:

$$C_{p(s)} = (1/m_s)[Q_s - Q_b]/\Delta T.$$

In that case, the c_p value is obtained by a difference of surface. That means that the result is not depending on fluctuations of the baseline between the different tests that can be seen with the previous technique.

2.5 The Calorimetric Techniques

The DSC technique, described in the previous paragraph, has a lot of advantages but also some drawbacks as soon as it is needed to work on larger amounts of sample, to investigate gas or liquid interactions, to simulate mixing or reactions between two or more components, to work with higher sensitivity.

A calorimeter is mainly characterized by a measurement chamber surrounded by a detector (thermocouples, resistance wires, thermistors, thermopiles) to integrate the heat flux exchanged by the sample contained in an adapted vessel. The measurement chamber is insulated in a surrounding heat sink, made of a high thermal conductivity material.

The main improvement with calorimetry is that it becomes possible to increase the size of the experimental vessel, and consequently the size of the sample without affecting the accuracy of the calorimetric measurement. According to this fundamental property, calorimeters of different sizes have been produced to adapt various types of applications. The calorimeter offers an experimental space in which different types of vessels are designed to especially make possible the investigations of interactions between solid and liquid materials.

2.5.1 Calorimetric Principles

Many different types of calorimeters are commercially available and most of the calorimetric principles are summarized in Table 2.4:

The main calorimetric modes can be resumed using Fig. 2.17, where:

- A is the sample contained in a vessel,
- B is the thermostated jacket (liquid or metallic),
- T_i is the temperature of the sample, and
- T_j is the temperature of the jacket.

Table 2.4 Different calorimetric principles

Property	Technique	Description
Heat	Isothermal calorimetry	In an isothermal calorimeter, a defined exchange of heat occurs between the sample and the surroundings at a given environment temperature. The heat flow rate is determined on the basis of the temperature difference along a thermal resistance between the sample and its surroundings.
Heat	Isoperibolic calorimetry	In an isoperibolic calorimeter, the temperature of the surroundings remains constant, while the temperature of the sample can differ from the surrounding temperature.
Heat	Adiabatic calorimetry	An adiabatic calorimeter is used to study chemical reactions and is one in which there is no net heat gain or loss during the chemical reaction.
Heat	Calvet Calorimetry	A Calvet calorimeter is a heat exchanging calorimeter with a cylindrical type detector working in isothermal and scanning modes.
Heat	Titration calorimetry	In a titration calorimeter, a small volume of solution A is injected into the calorimetric vessel containing the solution B. The corresponding heat of interaction is measured.
Heat	Flow calorimetry	In a flow calorimeter, the sample is a flowing liquid.
Heat	Solution calorimetry	In a solution calorimeter the mixing of the samples is performed in a static (batch) mode.
Heat	Reaction calorimetry	A reaction calorimeter is designed for the investigation of reactions between liquids or solids. The calorimetric technique can be isothermal, isoperibolic or adiabatic.
Heat	Bomb calorimetry	A bomb calorimeter is designed for measuring heat of combustion. The sample is contained in a heavy-walled metal container containing oxygen under pressure, followed by ignition to obtain the heat of combustion of the sample.

In the isothermal mode, the sample temperature T_i has to remain constant. To reach this target, the temperature of the jacket T_j is permanently adjusted. In this situation, a heat flux is measured between A and B and relates to any transformation or reaction that occurs in A.

In the adiabatic mode, the temperature of the sample T_i and the thermostated jacket T_j are kept at the same temperature in order to prevent any heat transfer between A and B. In that case, the temperature of the sample increases if the occurring reaction in A is exothermic or decreases if the reaction is endothermic.

The isoperibolic principle is an intermediate mode where the temperature of the thermostated jacket T_j is maintained at a constant temperature. The sample

Fig. 2.17 Sample and thermostated jacket in calorimetric principles
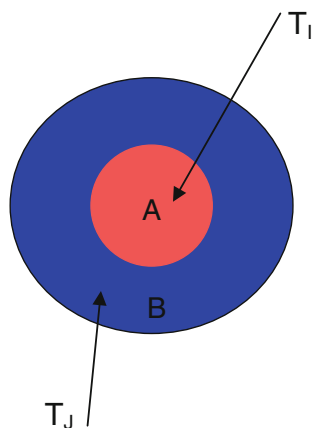
temperature T_i varies according to the transformation in A. The difference of temperature is measured and is related to the heat generated by the transformation.

According to the catalyst to be investigated or the catalytic process to be simulated, the calorimetric mode, and accordingly the type of calorimeter, has to be carefully selected.

2.5.2 Isothermal Calorimetry

The Calvet type calorimeter is one of the most commonly used for the catalytic investigations. Different types of experimental vessels have been developed to fulfill the different experimental requirements.

2.5.2.1 Calvet Principle

The Calvet principle has already been described in Sect. 2.4.2.

To understand the direct correlation between the electrical signal and the heat flux, it is needed to consider that a power W is fully dissipated in a calibration vessel surrounded by a fluxmeter composed of crowns of thermocouples (Fig. 2.11). An elementary power w_i is dissipated through each thermocouple producing an elementary variation of temperature ΔT_i between the internal and external weldings (Fig. 2.18):

$$w_i = \delta_i \Delta T_i \tag{2.13}$$

where δ_i is the conductance of the thermocouple.

The corresponding variation of temperature generates an elementary electromotice force (emf) according to the Oersted law:

Fig. 2.18 Joule effect calibration principle
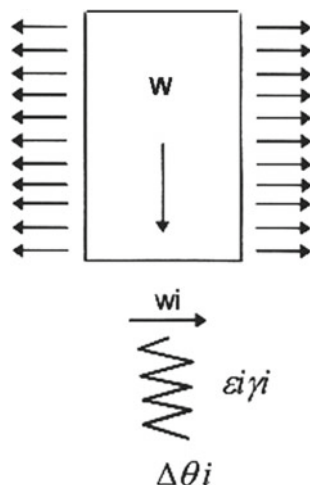
$$e_i = \varepsilon_i \Delta T_i \tag{2.14}$$

where ε_i is the thermoelectric constant of the thermocouple.

By combining the relations (2.13) and (2.14), and considering that all the thermocouples are in series:

$$E = \Sigma e_i = \Sigma(\varepsilon_i/\delta_i)_{w_i} \tag{2.15}$$

As all the thermocouples are identical and made from the same materials, the relation (2.15) can be expressed as:

$$E = (\varepsilon/\delta)\Sigma w_i \text{ or } E = (\varepsilon/\delta)W \tag{2.16}$$

The relation (2.16) shows that the power dissipated in the vessel is directly correlated to the heat flux. The term ε/δ corresponds to the calibration factor of the calorimeter. This relation provides the correlation between the electrical output of the calorimetric detector and the corresponding heat flux exchanged with the sample.

The main advantages of this type of calibration:

- it is an absolute calibration;
- it is not needed to use metallic reference materials;
- the calibration can be performed at a constant temperature, in the heating mode and in the cooling mode;
- it can apply to any experimental vessel volume; and
- it provides a very accurate calibration of the calorimetric detector.

According to the Calvet principle, many different calorimeters have been designed with various temperature ranges, from small to large size volumes, with a large variety of sensitivity. In the next paragraph is more precisely described one Calvet

calorimeter, produced by the SETARAM company, and that is used worldwide for catalytic investigations.

2.5.2.2 The C80 Microcalorimeter

The C80 microcalorimeter (produced by the SETARAM company) is a versatile tool in the field of catalytic investigations as it works according to different calorimetric modes:

- Isothermal calorimetry.
- Scanning calorimetry.
- Gas adsorption calorimetry.
- Liquid adsorption calorimetry.
- Mixing calorimetry.
- Percolation calorimetry.
- Reaction calorimetry.
- Pressure calorimetry.

In a Calvet calorimeter, the most important part is the thermoelectric element that provides the performances of the calorimetric detector.

The microcalorimeter is built around a high metallic conductive block with two cavities containing the thermopiles. Each thermopile is made of crowns of thermocouples, mounted on a metallic tube, and defines the experimental zone (Fig. 2.19). The two thermopiles (measure and reference) are inserted in a thermostated heating block that fixes the temperature of the calorimeter (Fig. 2.20). The block itself is surrounded by the heating element and arranged in an insulated chamber. The detectors define the experimental zone, in which the vessels are very tightly introduced. The top of the calorimeter is removable in order to make possible the fixation of dedicated vessels (mixing) inside the calorimeter and also for the arrangements of temperature pre-stabilisation features for fluid samples before introduction in the calorimetric zone.

The microcalorimeter is characterized by a large experimental volume ($15 \, cm^3$) that has allowed the design of a large variety of experimental vessels according to investigations to be carried out.

The main characteristic of the calorimeter is to be fitted on a rotating mechanism. A special mixing vessel has been designed to be used in such experimental conditions.

The microcalorimeter offers a large choice of experimental vessels according to the applications to be run:

- Isothermal and scanning calorimetry.

  - The batch standard vessel is designed for investigating any type of transformation at a constant temperature, when heating or cooling large volume of samples in the solid or liquid form. It is also dedicated to the determination of heat capacity.

- Pressure calorimetry

Fig. 2.19 Cross-section of
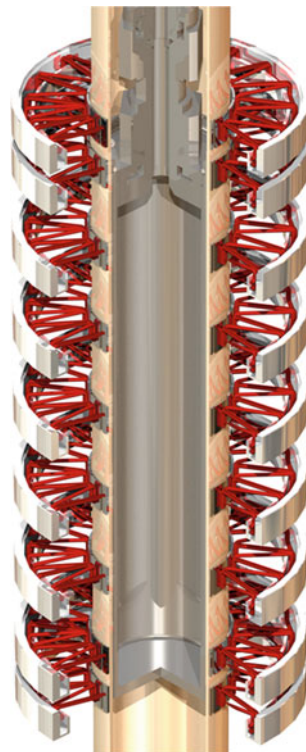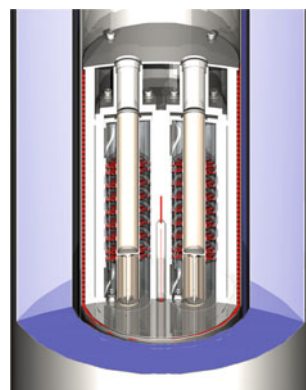the C80 thermopile

Fig. 2.20 Cross section of the
calorimeter

– The batch high pressure vessel is designed for the simulation of reaction and
  decomposition under pressure in a closed vessel or under controlled pressure
  (max : 100 bar). It is used to define the safety conditions of reaction operations
  but also investigations under supercrital gas conditions (e.g. adsorption of CO_2
  on zeolites).

A dedicated very high pressure vessel (max 350 bar) is connected to a high sensitivity pressure sensor through a special capillary tube. This vessel allows to record simultaneously the heat and pressure released by the sample during the reaction as a function of time or temperature [32].

For studies of adsorption at very high pressures (e.g. formation of gas hydrates), specific vessels are able to operate up to 1000 bar.

- Gas adsorption calorimetry.

    – The gas circulation vessel is fitted with two coaxial tubes and is used to produce a circulation of gas (inert or active) around the sample. It is especially convenient for the investigation of adsorption/absorption on a catalyst under normal pressure of reactive gas such as hydrogen, ammonia, CO, . . . [18, 22, 35] or high pressure [15].

    Such a vessel can also be fitted with a relative humidity generator in order to introduce a humid gas with a known rate of humidity on a solid sample.

This type of vessel has especially been used by Auroux [5, 14] to adapt a volumetric gas line to the calorimeter that is described on Fig. 2.21. Using such a calorimetric and volumetric device, the determination of the surface acidity and basicity of various types of zeolites and related materials was performed [6].

- Mixing and reaction calorimetry.

- The mixing vessel using the rotating mechanism is divided in two chambers and separated by a metallic lid (Fig. 2.22). The two materials are placed, one in the
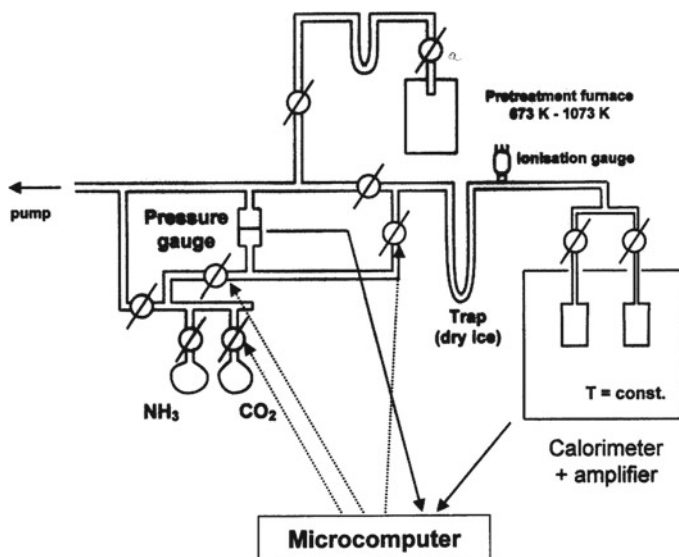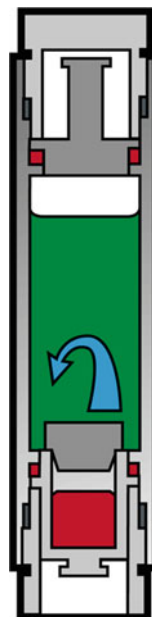

**Fig. 2.21** Calorimetric et volumetric devices coupling (from Ref. [14])

lower chamber (i.e. powder) and the other in the upper chamber (i.e. liquid). The mixing of the two components is obtained by rotating the calorimeter, the metallic lid acting as a stirrer. This mixing vessel is designed for investigating any liquid–liquid mixing (dilution, neutralization, reaction, . . .), solid–liquid mixing (dissolution, hydration, wetting, reaction, . . .)

– The membrane mixing vessel is especially dedicated to the mixing of viscous samples and for applications when the rotation of the calorimeter cannot be used. In such a vessel, the separation between both chambers is performed with a very thin membrane (metal or PTFE) (Fig. 2.23). The vessel is fitted with a metallic rod that is operated from outside the calorimeter. In this situation, the mixing of both components is obtained by pushing the rod in order to break the membrane. The rod is also used as a stirrer during the test. The applications are similar to the ones previously described.

• Sorption calorimetry.

   – The ampoule sorption vessel is designed for slow dissolution process and for wetting operation [43, 56]. The sample is introduced inside a special glass ampoule the upper part of which is connected to a vacuum pump and the bottom part of which is very thin. After outgassing during 30 min, the ampoule is sealed with a torch and the upper part of the ampoule is cut and withdrawn. The vacuum operation allows desorbing the surface of the solid sample (especially powder) and makes easier the interaction. The sealed ampoule is introduced in the vessel

Fig. 2.23 Mixing vessel
(metallic membrane)
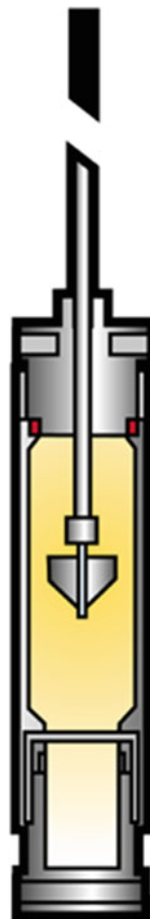
containing the solution. By breaking the ampoule using a piston rod, the solid
and liquid samples are put into contact

- Percolation calorimetry.

  – The percolation vessel is used for adsorption of liquid on a powder (especially
    catalyst) [41]. However when a liquid is flowed through a powder, the first
    interaction that occurs is wetting of the powder followed by adsorption. In
    order to make distinct these two thermal interactions, a special calorimetric
    design has been developed with the percolation vessel. The powder is introduced
    in a metallic cylinder on a sintered metallic section. A first carrier liquid is
    flowed through the powder to get the wetting (Fig. 2.24). Then the pump is
    switched to the liquid solute for the adsorption phase. According to the reaction,
    it will be possible to be back with the first carrier liquid in order to proceed
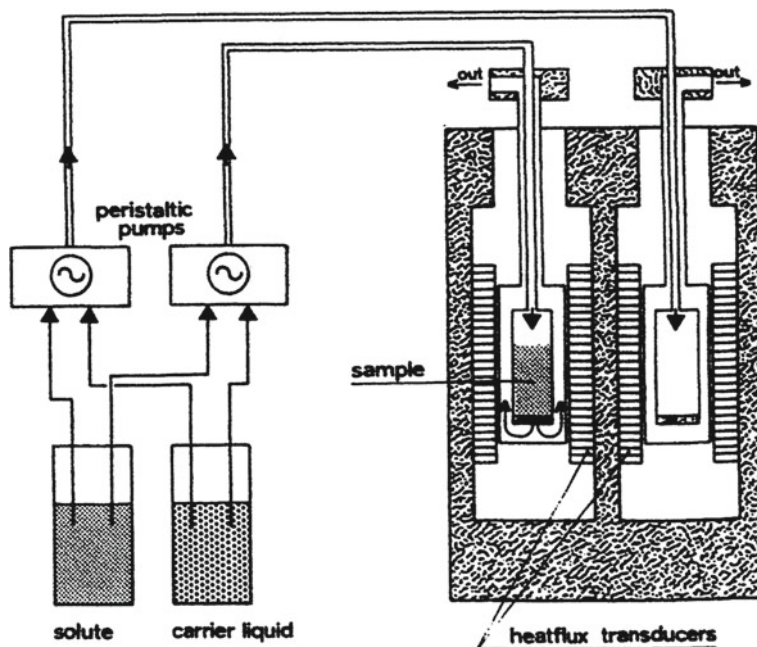
Fig. 2.24 Experimental set-up for percolation calorimetry

to the desorption phase. This calorimetric vessel is very convenient for the investigations of surface reactivity, catalyst contamination, chemisorption under normal and high pressure.

- Flow mixing calorimetry.

  – The use of the chemical sorbents is today one of the most popular absorption technique for the CO_2 capture in postcombustion techniques. In such an industrial process, the amine solution is introduced at the top of an absorption tower while the exhausted fume containing carbon dioxide is introduced at the bottom. As an intimate contact is reached in the absorption tower, the amine solution chemically absorbs the carbon dioxide from the gaseous stream. Such a process especially requires two types of thermodynamic parameters: gas solubility and enthalpy of absorption. The enthalpy of absorption, according to the amount of absorbed gas and the corresponding heat capacities of solutions, define the temperatures of the fluids when they exit the absorption columns. Flow mixing calorimetry is the ideal technique for measuring such enthalpies of absorption [2, 28]. In order to work under pressure, a dedicated high pressure mixing vessel is adapted to be used on the Setaram C80 calorimeter. The mixing vessel is made of a stainless steel tube in a helicoidal shape into a cylindrical container (Fig. 2.25). The length of the tube in closed thermal contact with the cylinder is about 240 cm. The fluids (CO_2 and amine solution) are introduced at the bottom

Fig. 2.25 The high pressure
flow mixing vessel
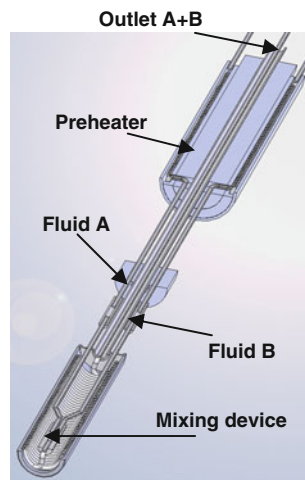
part of the vessel in two vertical and concentrical tubes. The mixing (dissolution, reaction) starts when the thinner part of the tube is reached. The heat that is associated with the reaction, is exchanged between the rolled tube and the calorimetric block through the wall of the vessel in an isothermal mode.

The flow mixing vessel operates from room temperature to $200\,°C$ and for a range of fluid pressure from 0.1 to 20 MPa. The fluid flowrates vary from 50 to $1500\,\mu \cdot min^{-1}$, that allow to cover a wide range of mixture composition.

2.5.3 Isothermal Titration Calorimetry

The different mixing vessels that are described in the previous paragraph are designed for the interaction between two components and are not well adapted for titration studies. In the Isothermal Titration Calorimetry, aliquots of sample B is added in a volume of sample A, located in the calorimetric vessel and maintained under a constant stirring (Fig. 2.26).

Another sample C can also be added according to the reaction to be simulated. To allow such experimentations, the C80 calorimetric block is modified to adapt a magnetic stirring system at its bottom part. This leaves more space to adapt the different liquid and gas introduction lines. A heating cover has also to be used for the thermostatisation of the fluids at the temperature of the calorimeter. The liquids are introduced through a motor-driven syringe pump that allow a continuous or a step injection of defined volumes.

Such a calorimetric technique is especially designed to follow the liquid adsorption of organic compounds on catalysts or zeolites [12, 21, 49]. The adsorption of n-butylamine (in decane) on a zeolite (in a solution of decane) illustrates the calori-

Fig. 2.26 Principle of the
Titrys calorimeter
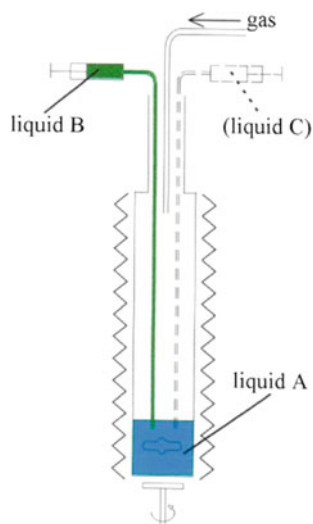
metric titration mode. After activation of the zeolite at 400 °C, the calorimetric test
is run at 40 °C. Aliquots of 0.25 ml of adsorbant are added until the saturation of the
zeolite is reached (Fig. 2.27).

Such a vessel is adapted to follow an organic reaction when several compounds
have to be added during the process.
It is also used to simulate the injection of very small amounts of water to produce a
hydrolysis reaction (hydrolysis of ammonia borane for the production of hydrogen).

2.6 The Thermogravimetric Technique

2.6.1 Principle

Thermogravimetric Analysis (TGA) or Thermogravimetry (TG) is defined as fol-
lowed by ICTAC: "A technique in which the mass of the sample is recorded versus
time or temperature while the temperature of the sample is programmed, in a con-
trolled atmosphere. The instrument is called a thermogravimetric analyzer (TGA) or
a thermobalance." [17].

Two different types of transformations can occur:

- Transformation with a mass loss: dehydration, dehydroxylation, evaporation,
  decomposition, desorption, pyrolysis, ...
- Transformation with a mass gain: adsorption, hydration, reaction, ...

The Fig. 2.28 shows a classical mass loss with the determination of the derivative
curve (DTG).
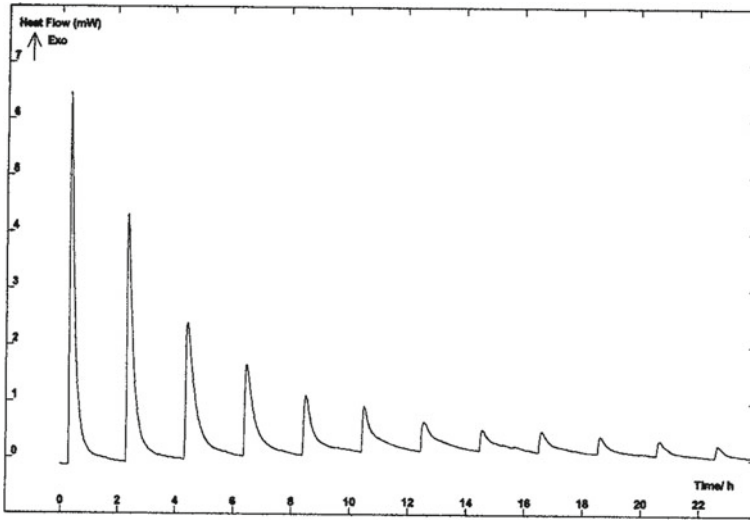
Fig. 2.27 Adsorption of n-butylamine (in decane) on a zeolite at 40 °C

Fig. 2.28 A TG mass loss curve with the derivative curve (DTG)
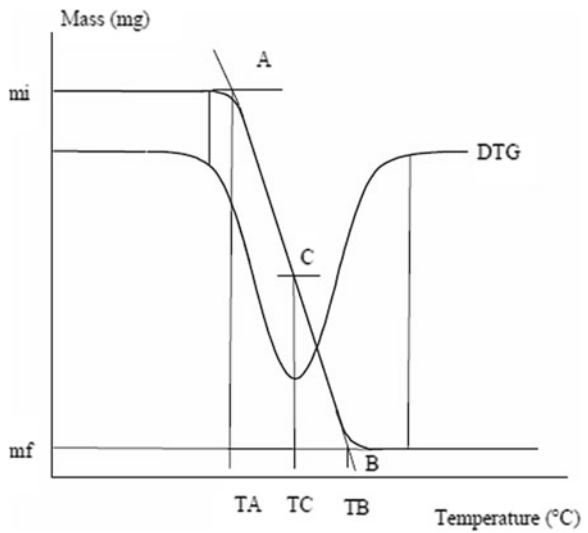
If m_i is the initial mass and m_f the final mass, the mass loss is equal to $(m_i - m_f)$ or $(m_i - m_f)/m_i$ in percentage.

It is interesting to notice that the DTG peak is very similar to the DTA/DSC peak (see also paragraph on couplings). The integration of the DTG peak also gives access to the variation of mass.

The DTG peak is related to the kinetics of the transformation, as the DTG signal corresponds to a mass variation rate. The shape of the peak directly informs on the rate of the transformation.

2.6.2 Detectors

Different types of TGA techniques are available and are described in Table 2.5.

A thermobalance is built around a highly sensitive balance module, a furnace and a controlled atmosphere cabinet. Different types of balance detectors are available but the most commonly used is based on the principle of the null position balance. An example is given in Fig. 2.29.

The balance is made of an articulated beam, suspended on a torsion wire. A rod is fixed in the middle of a beam and is coming with a window in the upper part. Four magnets are mounted in the middle part of the rod. Each of them is plunging in a solenoid fixed on the mechanical frame. On the same frame, a device of optical detection delivers a light that is fully crossing the slot of the window. The light signal is measured by means of a photodiode.

When there is a mass variation inducing a movement of the balance beam, the light is partially hidden. A compensation current is sent through the solenoids in order to have the beam back to the null position. With such a detection principle, the mass variation is proportional to the compensation current. It is positive or negative depending if it is a mass loss or a mass gain.

Based on this principle, different types of thermobalances are available: top loading balance, bottom loading balance, horizontal balance.

Table 2.5 Different types of TGA techniques

| Property	Technique	Description
Mass	Mono TGA	A technique in which the change of sample mass is analysed while the sample is subjected to a temperature variation. A mono TGA has only one furnace, for the sample.
Mass	Symmetrical TGA	A technique in which the change of sample mass is analysed while the sample is subjected to a temperature variation. A symmetrical TGA has two furnaces, one for the sample and one for the reference material.
Mass	High pressure TGA	A high pressure TGA is a TGA (mono or symmetrical) working with the test sample under pressure.
Mass	Corrosive TGA	A corrosive TGA is a TGA (mono or symmetrical) working with the test sample in a corrosive atmosphere.
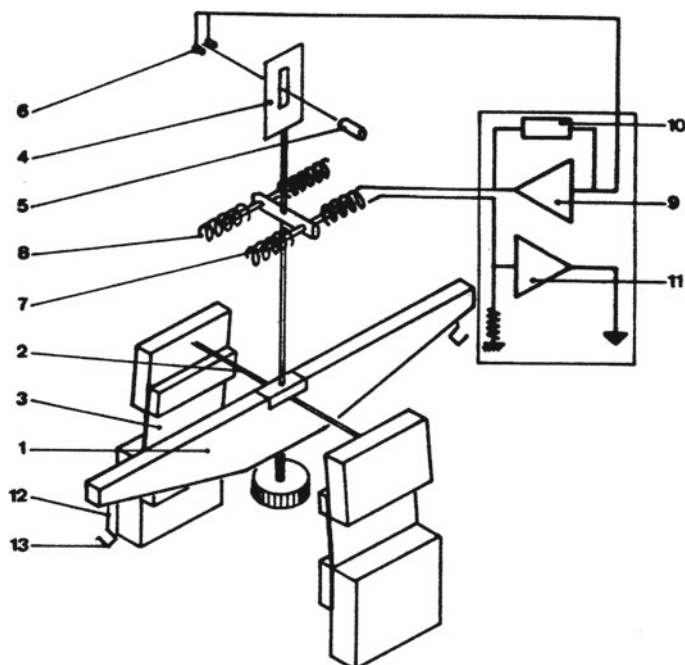
Fig. 2.29 Principle of a null position balance (SETARAM balance)

The nature of the furnace heating element depends on the range of temperature for the investigations. The most used materials are metallic (nickelchrome, kanthal, platinum, tungsten) but also SiC and graphite.

As for the DTA experimentation, the choice of the crucible for the TGA test has to be done very carefully. The main point is to select a material that will not react with the sample, especially at high temperature;

- Aluminum (up to 500 °C),
- Silica (especially used below 1000 °C as it is very inert and easy to clean),
- Alumina (especially required for metallic samples),
- Platinum (especially required for inorganic samples),
- Graphite and tungsten (for temperature above 1750 °C).

Other types of materials are available such as magnesia, zirconia, boron nitride, according to the sample under investigation.

2.6.3 Operation

2.6.3.1 Selection of the Atmosphere

As the crucible is open for the TGA test, the atmosphere around the sample has to be carefully controlled, especially in the case of catalysts. Different gas options are available to work in a thermobalance:

- Operation in inert gas:

  - This is the most common situation where it is needed to protect the sample from oxidation during the heating process. A vacuum purge is recommended prior to the introduction of the inert gas in order to empty the balance, the furnace and all the gas lines.
    If it is needed for desorbing the sample prior to the heating, a primary vacuum or even a secondary vacuum pumping is to be used for this operation before the introduction of the inert gas.
    Most of the investigations on catalysts need a good initial desorption of their surfaces before starting the adsorption investigations.

- Operation in reactive gas:

  - During catalytic investigations, different types of reactive gases are used and it is needed to know the risk of interactions with the different metallic and ceramic parts of the thermobalance. Here is the situation for the most common reactive gases:
    Air, oxygen for oxidation studies up to 1750 °C without specific problem.
    Reactive gas such as butane for investigations of catalytic reactions [36].
    Hydrogen: with such a gas two main concerns have to be considered: the concentration and the corrosion.
    A non-explosive mixture of less than 4 % H_2 in an inert gas is recommended. For higher concentrations, a safety device is required on the thermobalance. The use of H_2 requires that no trace of air is present in the thermobalance to avoid an explosion.
    Above 1000 °C, H_2 becomes a poison for platinum that is becoming brittle. The platinum–rhodium temperature control thermocouple has to be replaced to work above this temperature. Tungsten rhenium thermocouple is one option.

- Operation in corrosive gas:

  - Adsorption or reaction under corrosive gas, such as CO, NH_3 but also halogens (chlorine, fluorine), can be investigated using the TGA technique but caution has to be taken to avoid the contact between the corrosive gas and any metallic part of the thermobalance (especially the thermocouple).
    Dedicated experimental set-up need to be used to guarantee such a protection, as described on Fig. 2.30. A silica tube, with a restriction in the lower part, is introduced in the furnace. This tube shape allows having the thermocouple out

Fig. 2.30 TGA corrosive set-up
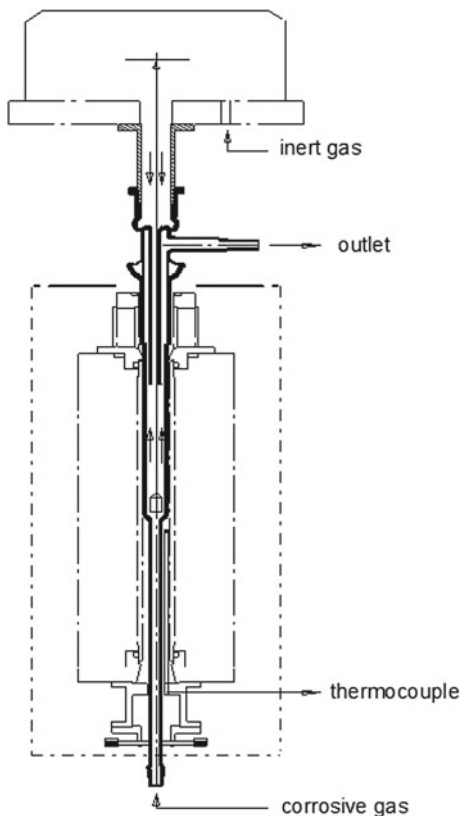
of the corrosive gas stream. The protection of the balance has to be carried out with an inert gas. The crucible and the suspension also are in silica. With such an adaptation it is possible to work with TGA with any type of corrosive gas, even at high concentration up to 1000 °C.

- Operation in humid atmosphere:

  – Adsorption of water vapour at a given pressure or at a relative humidity percentage is an important test to characterize the capabilibity of solid sorbents to fix water. It is also known that water vapour will enhance the adsorption of CO_2 on solid sorbents.
  To perform such a measurement a relative humidity generator has to be connected to the TGA through a thermostated gas line (Fig. 2.31).
  A dry gas is splitted in two lines, one remaining dry and the other one saturated with water. The two gas streams are mixed in a chamber. According to the desired relative humidity, the respective flowrates are adjusted for the gas mixture. The humid gas resulting from this operation is then transferred to the TGA via a heated transfer line.
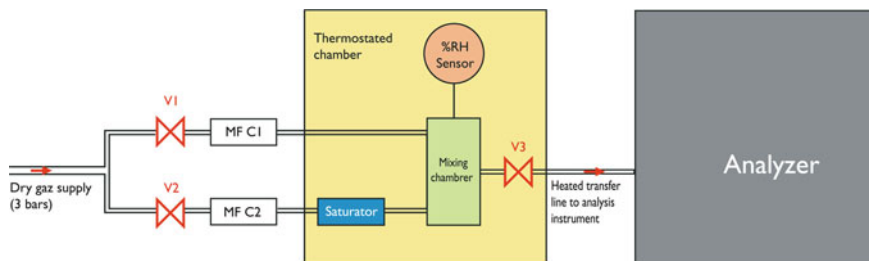
Fig. 2.31 Principle of the Wetsys relative humidity generator (Setaram)

2.6.3.2 Buoyancy Effect

The buoyancy effect is most of the time a problem that is misunderstood in the TGA measurement or often hidden by the numerical treatment of the TGA curves.

Buoyancy is the upward force exerted on an object when it is immersed, partially or fully, in a fluid (liquid or gas). Its value is equal to the weight of the fluid displaced by the object. In the case of the TGA experiment with a given crucible (the object), this results in an apparent increase of the mass when the sample is heated. The effect is observed on all conventional balances. In fact the term buoyancy includes different parameters: the true buoyancy as described before, the convection currents, the gas flow drag effects, the gas velocity effects, the thermomolecular forces, the thermal effects on the balance mechanism.

The buoyancy, according to these differents factors, is especially significant at low temperature and will decrease at high temperature. When a mass variation has to be accurately measured at low temperature (for example water content), a correction of the buoyancy has to be performed. The common way is to run a blank test with an empty crucible with the same experimental conditions. However this numerical correction remains dependent on the reproducibility of such a blank curve and the correction is affected with a certain uncertainty.

Another way to solve the problem is to use a symmetrical thermobalance.

In such a configuration (Fig. 2.32), the crucibles containing respectively the sample and the inert reference material are hung on each side of the balance. One or two furnaces are used according to the symmetrical model.

If the gas flowrates are adjusted on both sides, the buoyancy effect coming from the sample and the reference, as it is identical, is compensated.

2.6.4 Applications

As described in the previous paragraphs, the TGA technique provides a wide range of applications for the investigation of catalysts and related material:

- Gas adsorption and desorption.

Fig. 2.32 A symmetrical dual
furnace thermobalance

- Decomposition.
- Dehydration and dehydroxylation.
- Oxidation.
- Preparation of catalysts.
- Regeneration of catalysts.
- Investigation under various reactive gas (H_2, CO, . . .).
- Investigation under relative humidity.
- Investigation under corrosive gas.

In a more general way, thermogravimetry, with simple and short experiments allow preliminary screenings of catalysts where multiple variables are being considered. In just one experiment, the capacity of an adsorbent can be evaluated over an entire temperature range. It is also possible to collect qualitative information about the initial adsorption rates. Thermogravimetry, which has been applied to the preparation and characterization of adsorbents, has also proved to be a useful technique for preliminary adsorption capacity assessment. This is especially the case for the CO_2 capture performance of the sorbents and their thermal stability. For example, the evaluation of aminated solid sorbents for the CO_2 capture performance was evaluated [47].

Thermogravimetry is a very useful tool to evaluate the performances of catalytic filters used for the removal of soot from diesel exhaust gas [42].
TGA is also very widely used to investigate the NO_x-carbon reactions to control the emission of NO_x during the combustion process [60].

More recently, thermogravimetry has been applied to the evaluation of the chemical-looping combustion (CLC) process. It is considered as an energy-efficient method for the capture of carbon dioxide from combustion and provides an advantage of no energy loss for CO_2 separation without NO_x formation. This process consists of oxidation and reduction reactors where metal oxides particles are circulating through these two reactors [29, 54, 58]. The TGA set up for such an application is described on Fig. 2.33.

2.7 The Simultaneous Techniques

The TGA technique provides information on the mass variations that occurs within the sample, but most of the time, if the composition of the sample is unknown, the interpretation of the data are not easy. This is why the TGA technique is mostly used combined with other techniques such as DTA or DSC [59].

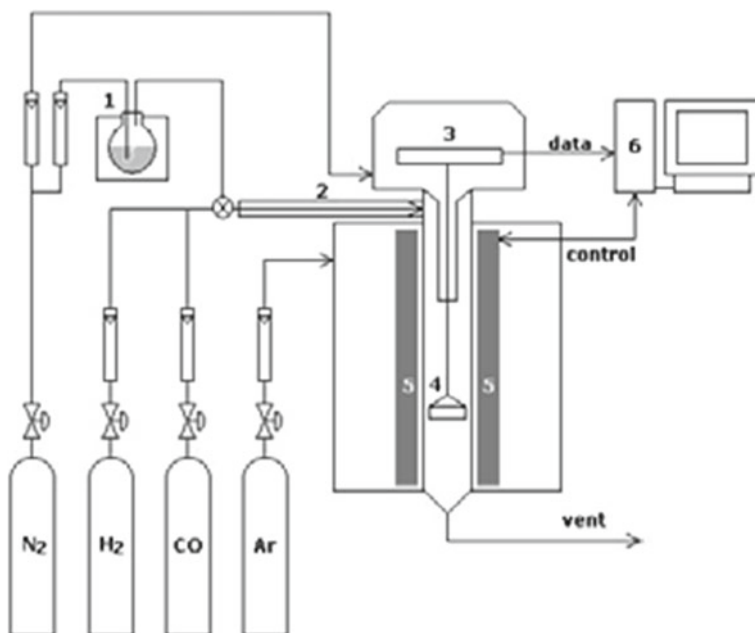**Fig. 2.33** Schematic diagram of a thermal gravimetric analyzer (TGA) system for the reactivity test; **1** water reservoir and bubbler, **2** gas pre-heater, **3** electric balance, **4** sample basket, **5** heater, **6** personal computer (from Ref. [29])

The TG-DTA or TG-DSC combination allows obtaining the simultaneous TGA and DTA or DSC measurements on the same sample (Fig. 2.34). The heat effects are correlated with the mass variations. The DTA or DSC signal gives information on heat effects not correlated with mass variation (melting, phase transitions, …)

The main interest of such a simultaneous measurement is that only one sample is used. This is especially very important for the characterization of catalysts as sample size (mass, surface, porosity, and composition), the gas flowrate and composition are critical parameters for an accurate determination.

Another important factor of the combination is that any endo or exo effect is related to the mass fraction that has been adsorbing or reacting.

The derivative DTG curve is similar to the DTA or DSC curve for the transformation with mass variation. Both curves are used for the kinetic interpretation of the sample transformation.

As an example of the interest of such a coupling technique, the investigation of the hydrogenation of a poisoned catalyst is given (Fig. 2.35).

A sample of dead catalyst is heated under pure hydrogen using a protected DTA rod. The combination of both techniques allows to understand the different processes that are occurring during the regeneration reaction:

- The first mass moss is associated with a small endothermic effect corresponding to the degradation of the organic compounds adsorbed on the catalyst.
- The second mass loss gives rise to a significant exothermic effect, due to the reduction of sulphur contained in the poisoned catalyst and producing H_2S.

The applications of the TG-DTA (or DSC) technique are very similar to the ones developed in the previous paragraph. However the DTA (or DSC) technique allows to give more information on the thermal properties of the catalyst, for example the characterization of materials after synthesis [1, 3, 27].

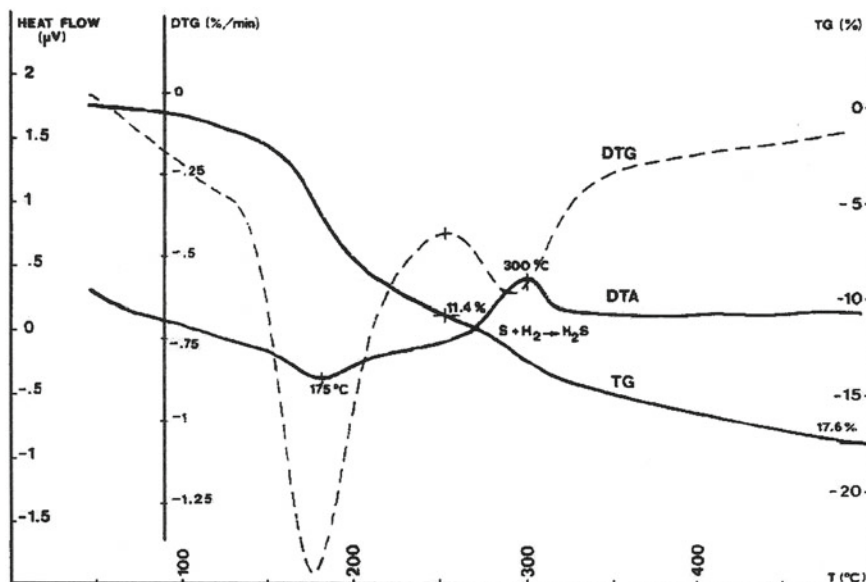**Fig. 2.34** The TG-DTA (or DSC) curve
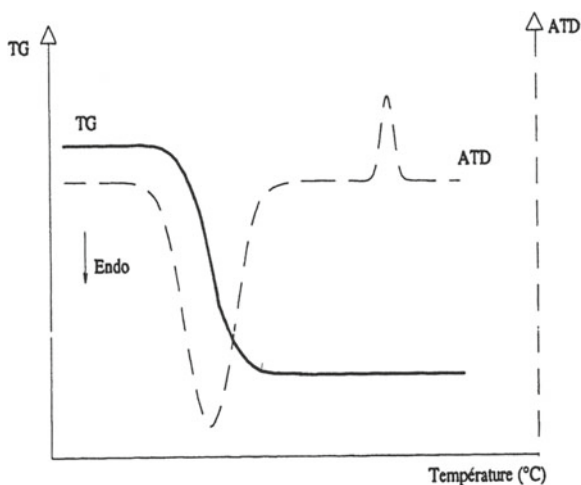
Fig. 2.35 TG, DTG and DTA curves of the hydrogenation of a poisoned catalyst

In most TG-DTA or DSC instruments, the DTA or DSC probe is attached to the balance. Such a combination results in a reduction of the performances of the TGA and the DTA or DSC detectors compared to the characteristics when they are used alone.

The Sensys TG-DSC is an exception in the field as the TGA and the DSC detectors are not mechanically attached (Fig. 2.36).

The Sensys TG-DSC is based on the Calvet type DSC (Fig. 2.36) used in the vertical position [30]. On top of the DSC, is adjusted a symmetrical balance corresponding to the principle described on Fig. 2.29. The crucibles containing the sample and the inert material are hung on each side of the balance and introduced in the calorimetric zone of the DSC without touching the walls. In such a situation, the crucibles are fully surrounded by the fluxmeters, providing an accurate DSC determination. In the same time, the symmetrical balance allows a compensation of the buoyancy effect resulting on a very high sensitive TG determination.

This technique is very powerful for the investigation of gas interaction on solid or liquid sample, such as adsorption, absorption, desorption, catalytic reaction under various types of gas (inert, oxidative, reducing, corrosive, humid) [55], the synthesis and catalytic behaviour of catalysts [53].

An example of the use of such a TG-DSC combination is given on the adsorption and desorption of CO_2 on a catalyst (Fig. 2.37). After preparation of the sample under helium, a mixture of helium (90 %) and CO_2 (10 %) is introduced on the catalyst. The exothermic effect is related to the amount of CO_2 adsorbed on the catalyst. When

Fig. 2.36 Cross section of the Sensys TG-DSC
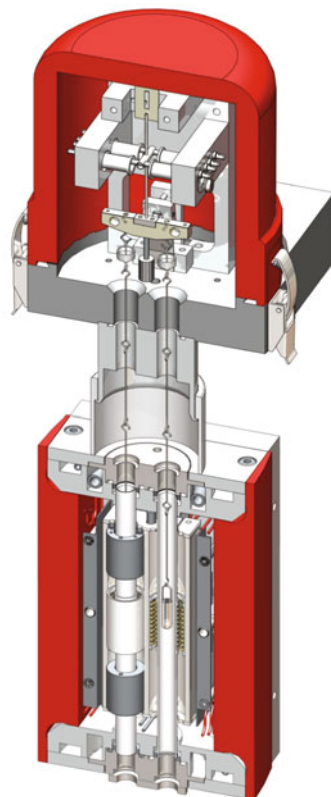
switching back to helium, it is noticed that desorption of the catalyst is not complete at this temperature.

The TG-DSC technique was also used for the investigation of amminoborane for the production of hydrogen [7]

2.8 Evolved Gas Analysis

Evolved Gas Analysis (EGA) is defined as followed by ICTAC:

"A technique of determining the nature and amount of volatile product or products formed during thermal analysis." [40].

As indicated in the previous chapter, the TGA technique only informs on the variation of sample mass, but hardly on the mechanisms linked to the decomposition or the reaction. The idea behind the EGA coupling is to analyze the vapours emitted by the sample during the test [39]. Three main gas coupling techniques are used for such an investigation as described in Table 2.6:
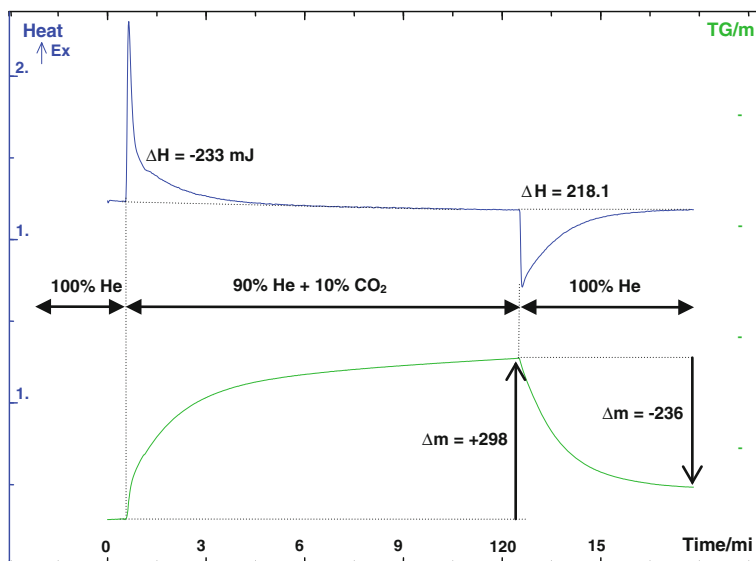
Fig. 2.37 Adsorption/desorption of CO_2 on a catalyst at 40 °C (Sensys TG-DSC)

Table 2.6 The main EGA techniques

Mass and MS spectrum	TGA-MS	In TGA-MS, the TG is connected online with a mass spectroscopy detector to determine the nature and amount of volatile product emitted by the sample during a thermogravimetric experiment
Mass and FTIR spectrum	TGA-FTIR	TGA-FTIR is a thermogravimetric analyzer (TGA) coupled online with a Fourier-Transform Infrared (FTIR) spectrometer to determine the nature and amount of volatile product emitted by the sample during a thermogravimetric experiment
Mass and GC chromatogram	TGA-GC	In TGA-GC, the TGA is connected online with a gas chromatograph(GC) detector to determine the nature and amount of volatile product emitted by the sample during a thermogravimetric experiment

2.8.1 TG-MS Coupling

During a long period, the main difficulty in the TG-MS coupling has been to define the right interface that will solve the following technical coupling problem:

- Pressure in the balance is equal to 1 bar, and about 10^{-6} bar in the mass spectrometer. The pressure has to be reduced by 6 decades during the gas transfer.
- Gas sampling has to be representative of the gas emitted by the sample.
- Emitted gas has not to be degradated in the transfer line.
- Condensation of the emitted gas have to be prevented in the transfer line.
- Time of gas transfer has to be short (about 100 ms) in order to have a simultaneous information between the TGA and the MS curves.

To solve these different technical requirements, two different interfaces are today available, according to the mass analysis to be performed:

- the capillary interface, and
- the skimmer or supersonic interface.

2.8.1.1 The Capillary Interface

The transfer line is made of a very thin silica capillary contained in a heated jacket to prevent the condensation, especially at the outlet of the furnace (Fig. 2.38). A fraction of the gas emitted by the sample is picked as closed as possible from the

Fig. 2.38 The heated capillary interface (Setaram)

Alumina tube

Sample

Graphite heating element

Graphite felt sleeve

Gas sampling tube

Regulation thermocouple

Capillary

To the mass spectrometer
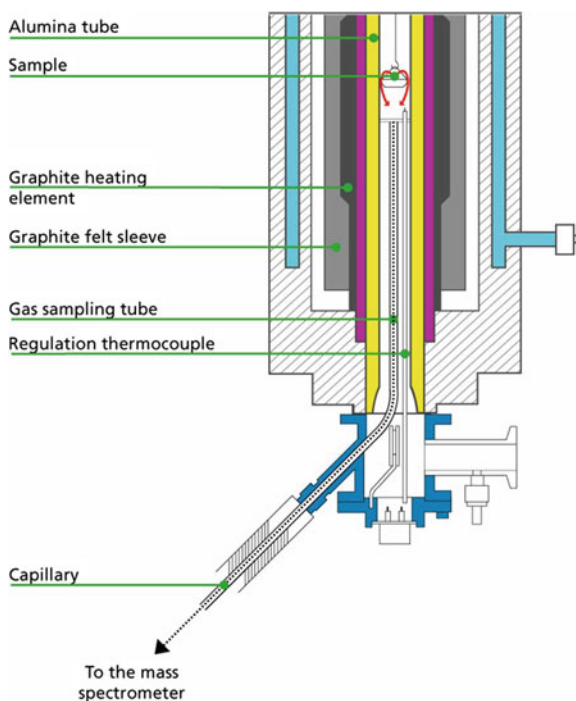
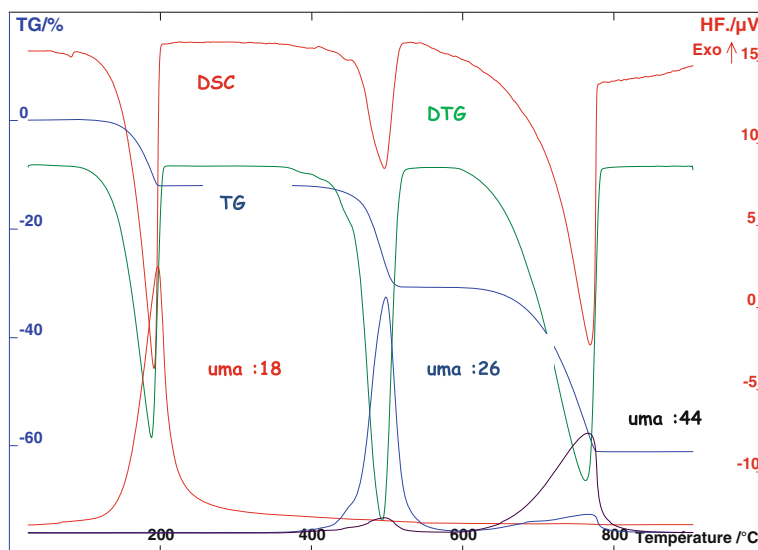**Fig. 2.39** TG, DTG, DSC and MS curves of the calcium oxalate decomposition. TG and FTIR curves of the calcium oxalate decomposition

TGA crucible to avoid gas dilution. The gas is then transferred through the capillary towards the MS detector within 100 ms.

The MS detector will provide a spectrum for each injection. According to the sample under study in the TGA, two situations can occur:

- The nature of the sample is known and it is possible to predict the types of gas that will be emitted by the sample during the TGA experiment. For such a test, characteristic mass numbers (amu), corresponding to the emitted gas, are selected and their variation is recorded versus time to be correlated with the TGA and DTG curves.
- The nature of the sample is unknown. In that case, it is needed to investigate the different MS spectra, especially at temperatures (times) corresponding to the different mass variations. When the significant mass numbers (amu) are identified, their variation can be drawn as described previously.

An example of the use of the heated capillary is given with the investigation of calcium oxalate CaC_2O_4, H_2O (Fig. 2.39)

The different uma traces show very clearly and respectively the different transformations that are expected and seen on the TG and DSC curves:

- the decomposition of the hydrate (H_2O^+);
- the decomposition of calcium oxalate in calcium carbonate (CO^+); and
- the decomposition of the calcium carbonate in calcium oxide (CO_2^+).

However the MS curves also allow to detect some CO_2 emission during the decomposition of the oxalate, and some CO during the decarbonatation.

It indicates the presence of some traces of air in the furnace that reacts with CO. Such a reaction is slightly seen on the DSC curve (small exothermic deviation at the end of the second endothermic peak) but it is not detectable on the TGA curve. This example, even based on a very common sample decomposition, shows the contribution of the MS coupling to the TG-DSC technique.

When coupled to MS, the thermogravimetric equipment can be used as a Temperature Programmed Oxidation (TPO) or/and a Temperature Programmed Desorption (TPD) technique to follow catalytic oxidation processes [62].
The TG-MS technique is also used to run Temperature Programmed Reduction (TPR) experiments in reducing atmosphere [10].

2.8.1.2 The Skimmer or Supersonic Interface

The capillary interface is easy to install but its use remains limited to a certain range of mass numbers. For high mass species (above 150 amu), condensation occurs in the transfer line. To avoid this problem, the skimmer, also called supersonic interface has to be selected.

Using a mass spectrometer in molecular mode requires to work under very low pressures, in order to avoid any saturation of the quadrupole and to make the production of the electron beam easier. Using the supersonic system, it is necessary to have an important difference of pressure between the thermobalance and the mass spectrometer, in order to obtain a free molecular beam.

A gas at a stable temperature and at atmospheric pressure is in a disturbed molecular state. The rates of the molecules have an isotropic distribution in the space, varying as the temperature square root varies. If a chamber under atmospheric pressure and a chamber under low pressure are connected together through a small hole, it is possible to obtain a thermal effusion or a supersonic beam. The isentropic pressure reduction enables the molecules to reach some supersonic speeds in a few micro seconds. Therefore, intermolecular recombinations are not possible and a molecular beam in only one direction is obtained. Pressure reduction releases the impact between the molecules.

On a technical point of view, the supersonic system is adjusted on the thermobalance furnace, in order to have the MS detector straight to the sample container (Fig. 2.40).
Gas emitted by the sample flows through a taking hole at the top of a first chamber working under primary vacuum. A second chamber, working under secondary vacuum, is located inside the first chamber. The secondary chamber receives a cone with a hole at the top. The chamber is in line with the quadrupole detector of the gas analysis system.

The Supersonic or skimmer system is more costly and more difficult to use but it gives many advantages on the capillary transfer line: no condensation in the transfer line, no collision between the molecules and with the transfer line wall, possibility to detect high mass species (above 500 amu)
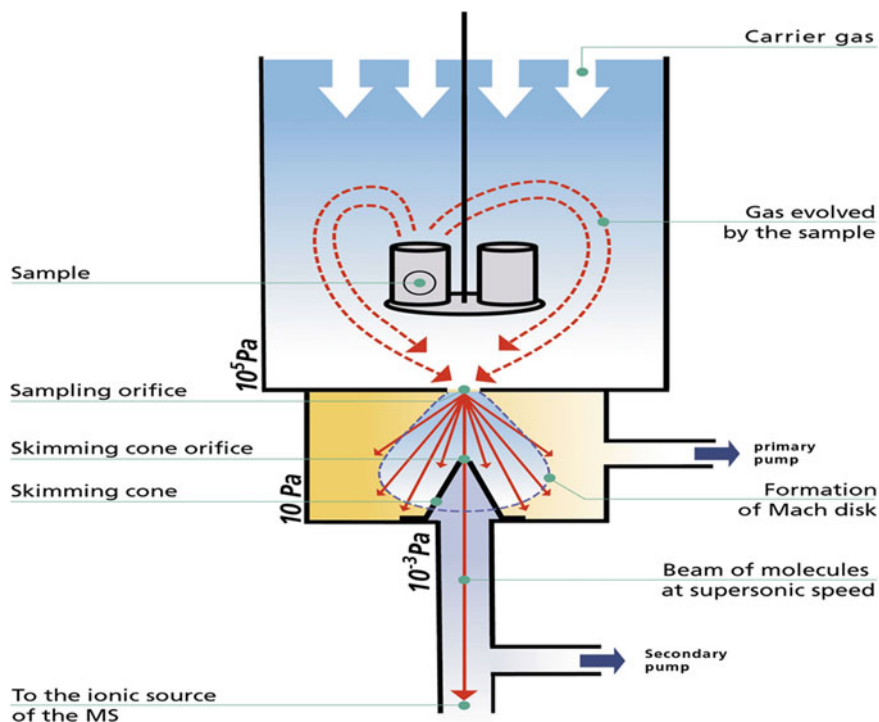
Fig. 2.40 The supersonic interface (Setaram)

2.8.2 TG-FTIR Coupling

The TG-FTIR coupling is easier to carry out as both analyzers are working at the same normal pressure. A heated transfer line has to be installed between the outlet of the thermobalance and the inlet of the FTIR spectrometer.

As in the TG-MS coupling, the time of transfer is very short. Caution has to be taken to avoid any condensation in the transfer line.

The infra red cell that is mostly KBr made of, has to be adapted (use of ZnSe cell) in order to avoid degradation with water vapour.

The same investigation of calcium oxalate, described previously with the TG-MS coupling, is used to see the difference between the two coupling techniques (Fig. 2.41).

The characteristic wavelengths of the expected emitted gas are recorded together with the three mass losses corresponding to the different steps of decomposition of the calcium oxalate:

- H_2O ($3734\,cm^{-1}$) for the decomposition of the hydrate.
- CO ($2068\,cm^{-1}$) for the decomposition of the calcium oxalate in calcium carbonate.
- CO_2 ($2359\,cm^{-1}$) for the decomposition of the calcium carbonate in calcium oxide.
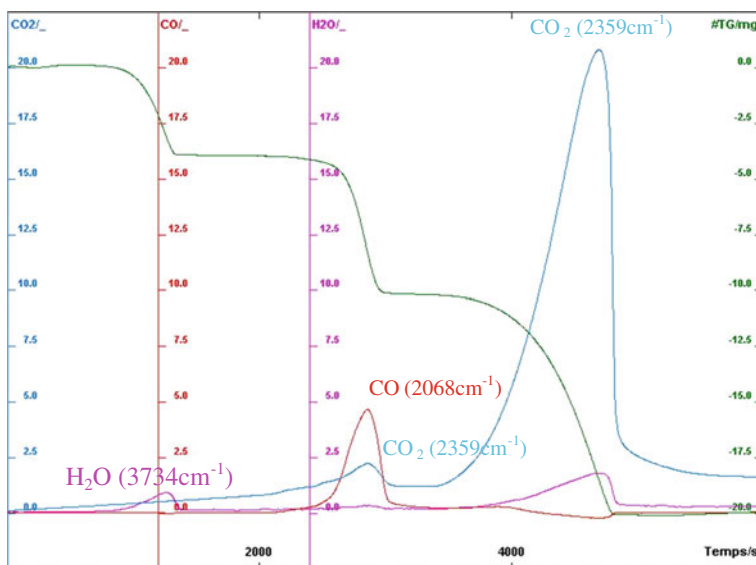
Fig. 2.41 TG and FTIR curves of the calcium oxalate decomposition

As seen before with the TG-MS coupling, a fraction of CO_2 is detected during the second loss, and a fraction of CO during the third mass loss, indicating the presence of some trace of air in the furnace during the experiment.

On such an example, very similar results are obtained with both EGA techniques.

2.9 Conclusion

The thermal analysis and calorimetric techniques provide a very large variety of possibilities of experimentations, of combinations with other analytic techniques that make unlimited the number of applications, especially in the field of characterization of catalysts and evaluation of catalytic processes.

The different techniques, together with the corresponding detectors and the experimental vessels, can be adapted and adjusted to the investigations of new materials or new processes. This is the case for example with the research on hydrogen storage on metal hydrides, all the works related to the capture and sequestration of CO_2 with the evaluation of solid and liquid sorbents, the development of the Chemical Looping Combustion with improved catalysts...

With this efficient faculty of adaptation to new research fields, the thermal analysis and calorimetric techniques are promised to a brilliant future

References

1. M.A. Aramendia, V. Borau, C. Jiménez, A. Marinas, J.M. Marinas, J.A. Navio, J.R. Ruiz, F.J. Urbano, Synthesis and textural-structural characterization of magnesia, magnesia–titania and magnesia–zirconia catalysts. Colloids Surf. A: Physicochem. Eng. Aspects **234**, 17–25 (2004)

2. H. Arcis, L. Rodier, J.Y. Coxam, Enthalpy of solution of CO_2 in aqueous solutions of 2-amino-2-methyl-1-propanol. J. Chem. Thermodyn. **39**, 878–887 (2007)

3. A. Arnold, M. Hunger, J. Weitkamp, Dry-gel synthesis of zeolites [Al]EU-1 and [Ga]EU-1. Microporous Mesoporous Mater. **67**, 205–213 (2004)

4. A. Auroux, Thermal methods: calorimetry, differential thermal analysis and calorimetry (Chap. 22), in *Catalyst Characterization: Physical Techniques for Solid Materials*, ed. by B. Imelik, J.C. Vedrine (Plenum Press, New York, 1994)

5. A. Auroux, Acidity characterization by microcalorimetry and relationship with reactivity. Top. Catal. **4**, 71–89 (1997)

6. A. Auroux, *Acidity and Basicity: Determination by Adsorption Microcalorimetry Molecular Sieves* (Springer, Berlin, 2006)

7. J. Baumann, F. Baitalow, G. Wolf, Thermal decomposition of polymeric aminoborane $(H_2BNH_2) \times$ under hydrogen release. Thermochim. Acta **430**, 9–14 (2005)

8. S. Bennici, A. Auroux, Thermal analysis and calorimetry methods, in *Metal Oxide Catalysis*, vol. 1, ed. by S.D. Jackson, J.S.J. Hargreaves (Wiley, Weinheim, 2009)

9. J.J.P. Biermann, P.P. Coelen, H. Den Daas, F.J.J.G. Janssen, The use of a heat-flow differential scanning calorimeter as a plug-flow fixed bed reactor in heterogeneous catalysis. Thermochim. Acta **144**, 329–337 (1989)

10. V.Y. Bychkov, Y.P. Tyulenin, V.N. Korchak, E.L. Aptekar, Study of nickel catalyst in oscillating regime of methane oxidation by means of gravimetry and mass-spectrometry. Appl. Catal. A: Gen. **304**, 21–29 (2006)

11. K. Chakarova, K. Hadjiivanov, G. Atanasova, K. Tenchev, Effect of preparation technique on the properties of platinum in NaY zeolite: a study by FTIR spectroscopy of adsorbed CO. J. Mol. Catal. A: Chem. **264**, 270–279 (2007)

12. F. Dan, M.H. Hamedi, J.P.E. Grolier, New developments and applications in titration calorimetry and reaction calorimetry. J. Thermal Anal. Calorim. **85**, 531–540 (2006)

13. J.L. Daudon, Heat flux devices and methods for optimum specific heat measurements, in *Fourteenth European Conference on Thermophysical Properties*, Lyon, France, 1996

14. L. Dussault, J.C. Dupin, E. Dumitriu, A. Auroux, C. Guimon, Microcalorimetry TPR and XPS studies of acid–base properties of NiCuMgAl mixed oxides using LDHs as precursors. Thermochim. Acta **434**, 93–99 (2005)

15. A.F.P. Ferreira, M.C. Mittelmeijer-Hazeleger, A. Bliek, Adsorption and differential heats of adsorption of normal and iso-butane on zeolite MFI. Microporous Mesoporous Mater. **91**, 47–52 (2006)

16. S.P. Felix, C. Savill-Jowitt, D.R. Brown, Base adsorption calorimetry for characterising surface acidity: a comparison between pulse flow and conventional "static" techniques. Thermochim. Acta **433**, 59–65 (2005)

17. P. Gallagher, Thermogravimetry and thermomagnetometry, in *Handbook of Thermal Analysis and Calorimetry*, vol. 1, Principles and Practice, ed. by M.E. Brown (Elsevier, The Netherlands, 1998)

18. A. Gervasini, P. Carniti, J. Kerainen, L. Niinisto, A. Auroux, Surface characteristics and activity in selective oxidation of o-xylene of supported V_2O_5 catalysts prepared by standard impregnation and atomic layer deposition. Catal. Today **96**, 187–194 (2004)

19. K. Habersberger, Application of thermal analysis to the investigation of catalysts. J. Thermal Anal. **12**, 55–58 (1977)

20. P.J. Haines, M. Reading, F.W. Wilburn, Differential thermal analysis and differential scanning calorimetry, in *Handbook of Thermal Analysis and Calorimetry*, vol. 1, Principles and Practice, ed. by M.E. Brown (Elsevier, The Netherlands, 1998)

21. M. Hart, G. Fuller, D.R. Brown, J.A. Dale, S. Plant, Sulfonated poly(styrene-co-divinylbenzene) ion-exchange resins: acidities and catalytic activities in aqueous reactions. J. Mol. Catal. A: Chem. **182–183**, 439–445 (2002)
22. M.P. Hart, D.R. Brown, Surface acidities and catalytic activities of acid-activated clays. J. Mol. Catal. A: Chem. **212**, 315–321 (2004)
23. T. Hatakeyama, Z. Liu, *Handbook of Thermal Analysis* (Wiley, New York, 1998)
24. W. Hemmiger, S.M. Sarge, Definitions, nomenclature, terms and litterature, in *Handbook of Thermal Analysis and Calorimetry*, vol. 1, Principles and Practice, ed. by M.E. Brown (Elsevier, The Netherlands, 1998)
25. International Confederation for Thermal Analysis, in *For Better Thermal Analysis and Calorimetry*, 3rd edn., ed. by J.O. Hill (RSC Publishing, Cambridge, 1991). http://www.ictac.org
26. ISO 11357-1, *Plastics: Differential Scanning Calorimetry—Part1: General principles*, (Universidade De Aveiro, Aveiro, 1997)
27. D.S. Kim, J.S. Chang, J.S. Hwang, S.E. Park, J.M. Kim, Synthesis of zeolite beta in fluoride media under microwave irradiation. Microporous Mesoporous Mater. **68**, 77–82 (2004)
28. D. Koschel, J.Y. Coxam, L. Rodier, V. Majer, Enthalpy and solubility data of CO_2 in water and $NaCl_{(aq)}$ at conditions of interest for geological sequestration. Fluid Phase Equilib. **247**, 107–120 (2006)
29. A. Lambert, C. Delquié, I. Clémençon, E. Comte, V. Lefebvre, J. Rousseau, B. Durand, Synthesis and characterization of bimetallic Fe/Mn oxides for chemical looping combustion. Energy Procedia **1**, 375–381 (2009)
30. P. Le Parlouër, Simultaneous TG-DSC: a new technique for thermal analysis. Thermochim. Acta **121**, 307–322 (1987)
31. P. Le Parlouër, C. Mathonat, Sensys: an innovative concept for the Calvet DSC111 and TG-DSC111, in *33rd NATAS Proceedings*, Universal City, USA (2005), p. 44
32. X.R. Li, H. Koseki, Hazard evaluation of self-decomposition materials by the combination of pressure and heat flux measurements. Thermochim. Acta **423**, 77–82 (2004)
33. R.C. Mackenzie, *Differential Thermal Analysis*, vols. 1, 2 (Academic, London, 1972)
34. E. Manova, T. Tsoncheva, C. Estournès, D. Paneva, K. Tenchev, I. Mitov, L. Petrov, Nanosized iron and iron-cobalt spinel oxides as catalysts for methanol decomposition. Appl. Catal. A: Gen. **300**, 170–180 (2006)
35. A. Maroto-Valiente, I. Rodrıguez-Ramos, A. Guerrero-Ruiz, Surface study of rhodium nanoparticles supported on alumina. Catal. Today **93–95**, 567–574 (2004)
36. V. Martin, J.M.M. Millet, J.C. Volta, Thermogravimetric analysis of vanadium phosphorus oxide catalysts doped with cobalt and iron. J. Thermal Anal. **53**, 111–121 (1998)
37. J.L. McNaughton, C.T. Mortimer, *Physical Chemistry Series*, vol. 2 (Butterworths, London, 1975)
38. J. Mercier, J. Thermal Anal. **14**, 161 (1978)
39. L. Meublat, P. Le Parlouër, Couplage thermogravimétrie: analyse de gaz. Spectra 2000 **19**(161), 59–62 (1991)
40. J. Mullens, EGA: evolved gas analysis, in *Handbook of Thermal Analysis and Calorimetry*, vol. 1, Principles and Practice, ed. by M.E. Brown (Elsevier, The Netherlands, 1998)
41. F.T.T. Ng, A. Rahman, T. Ohasi, M. Jiang, A study of the adsorption of thiophenic sulphur compounds using flow calorimetry. Appl. Catal. B: Environ. **56**, 127–136 (2005)
42. Y. Nguyen Huu Nhon, H.M. Magan, C. Petit, Catalytic diesel particulate filter: evaluation of parameters for laboratory studies. Appl. Catal. B: Environ. **49**, 127–133 (2004)
43. F. Omota, A.C. Dimian, A. Bliek, Partially hydrophobized silica supported Pd catalyst for hydrogenation reactions in aqueous media. Appl. Catal. A: Gen. **294**, 121–130 (2005)
44. J. Paulik, F. Paulik, in *Comprehensive Analytical Chemistry*, vol. 12, ed. by G. Svehla (Elsevier, Amsterdam, 1981)
45. B. Pawelec, J.L.G. Fierro, Applications of thermal analysis in the preparation of catalysts and in catalysis, in *Handbook of Thermal Analysis and Calorimetry*, vol. 2, Applications to Inorganic and Miscellaneous Materials, ed. by M.E. Brown, P.K. Gallagher (Elsevier, The Netherlands, 2003)

46. L. Pinard, J. Mijoin, P. Magnoux, M. Guisnet, Dichloromethane transformation over bifunctional PtFAU catalysts. Influence of the acidobasicity of the zeolite. C. R. Chim. **8**, 457–463 (2005)

47. M.G. Plaza, C. Pevida, B. Arias, J. Fermoso, A. Arenillas, F. Rubiera, J.J. Pis, Application of thermogravimetric analysis to the evaluation of aminated solid sorbents for CO_2 capture. J. Thermal Anal. Calorim. **92**(2), 601–606 (2008)

48. M.I. Pope, M.D. Judd, *Differential Thermal Analysis: A Guide to the Technique and its Applications* (Heyden, London, 1977)

49. V. Quaschning, A. Auroux, J. Deutsch, H. Lieske, E. Kemnitz, Microcalorimetric and catalytic studies on sulfated zirconia catalysts of different preparations. J. Catal. **203**, 426–433 (2001)

50. V. Rakic, V. Dondur, R. Hercigonja, Thermal effects of the interaction of carbon monoxide with zeolites. Thermochim. Acta **379**, 77–84 (2001)

51. M. Resan, M.D. Hampton, J.K. Lomness, D.K. Slattery, Effects of various catalysts on hydrogen release and uptake characteristics of $LiAlH_4$. Int. J. Hydrogen Energy **30**, 1413–1416 (2005)

52. M.J. Richardson, E.L. Charsley, Calibration and standardisation in DSC, in *Handbook of Thermal Analysis and Calorimetry*, vol. 1, Principles and Practice, ed. by M.E. Brown (Elsevier, The Netherlands, 1998)

53. R. Ruiz, C. Pesquera, F. González, C. Blanco, Synthesis and catalytic behaviour of heterogenized rhodium catalysts on modified clays. Appl. Catal. A: Gen. **257**, 165–175 (2004)

54. L. Shen, M. Zheng, J. Xiao, R. Xiao, A mechanistic investigation of a calcium-based oxygen carrier for chemical looping combustion. Combust. Flame **154**, 489–506 (2008)

55. S. Siffert, L. Gaillard, B.L. Su, Alkylation of benzene by propene on a series of beta zeolites: toward a better understanding of the mechanisms. J. Mol. Catal. A: Chem. **153**, 267–279 (2000)

56. J. Silvestre-Albero, C. Gomez de Salazar, Characterization of microporous solids by immersion calorimetry. Colloids Surf. A: Physicochem. Eng. Aspects **187–188**, 151–165 (2001)

57. P.F. Siril, A.D. Davison, J.K. Randhawa, D.R. Brown, Acid strengths and catalytic activities of sulfonic acid on polymeric and silica supports. J. Mol. Catal. A: Chem. **267**, 72–78 (2007)

58. S.R. Son, S.D. Kim, Semi-continuous operation of chemical looping combustion with metal oxides supported on bentonite in an annular fluidized bed reactor, in *Proceedings of the Asian Conference on Fluidized Bed and Three Phase Reactors* (2006)

59. J. van Humbeeck, Simultaneous thermal analysis, in *Handbook of Thermal Analysis and Calorimetry*, vol. 1, Principles and Practice, ed. by M.E. Brown (Elsevier, The Netherlands, 1998)

60. S. Wang, V. Slovak, B.S. Haynes, Kinetic studies of graphon and coal-char reaction with NO and O_2: direct non-linear regression from TG curves. Fuel Process. Technol. **86**, 651–660 (2005)

61. W.W. Wendlandt, *Thermal Analysis*, vol. 19, 3rd edn. (Wiley, New York, 1986)

62. J. Zhao, Z. Liu, D. Sun, TPO-TPD study of an activated carbon-supported copper catalyst-sorbent used for catalytic dry oxidation of phenol. J. Catal. **227**, 297–303 (2004)