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QUANTITATIVE DTA UNDER A CHANGED GAS ATMOSPHERE

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The present paper describes a method for experimental determination of the momentary values of the thermal analyser calorimetric sensitivity when the type of gas in the DTA cell is changed.

In a quantitative interpretation of DTA it is assumed that the temperature difference between the sample and reference crucibles (voltage signal ΔU if the differential thermocouple sensitivity is constant) is directly proportional to the momentary value of the heat flux $\mathrm{d}Q/\mathrm{d}t$ resulting from the sample heat capacity and the phase or chemical transformations taking place in the sample:

$$\frac{\mathrm{d}Q}{\mathrm{d}t}=\frac{\Delta U}{E}\cdot$$

The calorimetric sensitivity E of the thermal analyser (DTA apparatus) is a complicated function of many variables [1], and for steady conditions of experiments it is determined by a suitable calibration.

When the crucibles are separated from each other and from the furnace walls by a gas, the calorimetric sensitivity of such a type of DTA apparatus is strongly dependent on the thermal properties of this gas. It is self-evident that when the composition (properties) of the gas atmosphere inside the DTA cell is changed, the calorimetric sensitivity of the apparatus is changed too.

Generally, there are two main types of changes in the gas atmosphere composition during a DTA test:

(1) changes resulting from decomposition reactions or evaporation processes occurring in the sample,

(2) controlled changes of the composition or nature of the gas flowing through the DTA cell. In the first instance, intense rinsing of the DTA cell with an inert gas is used. Consequently, the volatile products are quickly removed from the sample crucible and the DTA cell alike. This takes precautions against essential changes of the calorimetric sensitivity. In the second instance, changes of the calorimetric sensitivity may be observed while the examined reaction is taking place. In this case the momentary values of the calorimetric sensitivity must be established and included in precise calorimetric calculations. The above situation arises for

example, during an isothermal examination of a solid – gas reaction, if a reactive gas is passed into the DTA cell instead of an inert one. This paper reports a method of performing suitable calibration for the latter case.

Principles

When gas 1 (inert) is exchanged for gas 2 (reactive), the calorimetric sensitivity E of the apparatus is dependent on time. It is convenient to describe this dependence by a temperature-independent time factor E_t. Then, the momentary values of E are the products of the momentary values of this factor and the temperature-dependent calorimetric sensitivity E_1 of the apparatus when gas 1 flows through its DTA cell:

$$E = E_1 \cdot E_t .$$

The fact that ΔU, measured while a thermally stable sample is heated at a constant heating rate V_T, is directly proportional to its capacity C_S [2, 3]:

$$C_S = \frac{\Delta U}{E \cdot V_T}$$

is utilized to determine the momentary values of the time factor. Two heat capacity measurements are required on the same sample: the first under a constant flow of an inert gas, and the second when the gases are exchanged. Values of the time factor can then be evaluated as quotients of suitable ΔU signals, measured at the same temperature (Fig. 1):

$$E_t = \frac{\Delta U_t}{\Delta U_1} .$$

When momentary values of the time factor, and consequently the calorimetric sensitivity *vs.* time, have been determined, the momentary heat flux values $(\mathrm{d}Q/\mathrm{d}t)_t$

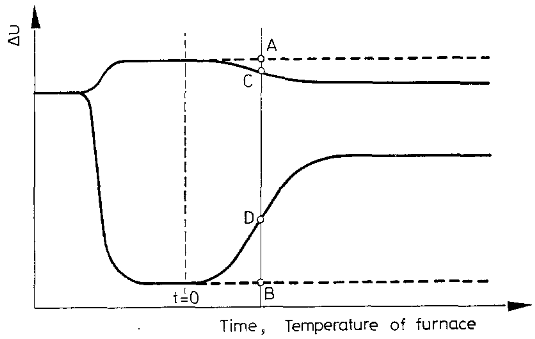

Fig. 1. Determination of the calorimetric sensitivity time factor on the basis of two heat capacity measurements on the same sample:
broken line – at a constant flow of gas 1 (inert)
full line – during the controlled exchange of gas 1 for gas 2 (reactive)
$AB = \Delta U_1$, $CD = \Delta U_t$

relevant to the examined reaction may be calculated from the following relationship:

$$\frac{dQ}{dt} = \frac{\Delta U_{t,r}}{E_1 \cdot E_t}$$

where $\Delta U_{t,r}$ is the ΔU value of the DTA curve at time t.

Experimental

The described manner of calibration has been applied to the quantitative isothermal DTA examination of the reduction run of nickel catalysts used for the hydrogenation of fatty acids to fatty alcohols [4].

A Mettler TA 2000A thermal analyser was used. Two gases (pure argon as inert and hydrogen as reactive) were connected to its DTA cell through a two-way selector valve and flow control regulator (Fig. 2).

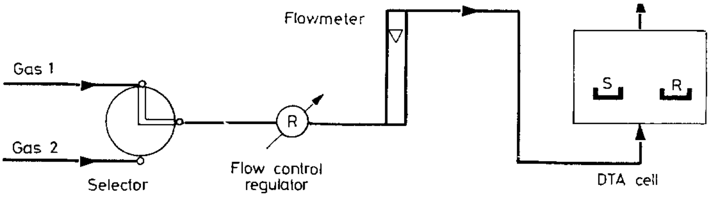

Fig. 2. Scheme of the gas supply pipe to the measuring cell

Catalysts were subjected to drying and oxidizing ignition before the examination. Ignited catalysts were weighted into open Al crucibles in amounts of about 20 mg. An empty crucible was used as reference. Crucibles were placed in the DTA cell and heated up to constant temperature (573 K) in flowing argon. Then, instead of argon, hydrogen was dosed into the apparatus with the same flow intensity, by turning the selector valve (time $t = 0$).

The calorimetric sensitivities of the apparatus at 429.7 K were determined in flowing argon and hydrogen alike, on the basis of the fusion of high-purity indium. Its temperature-dependence [5] was taken into account to calculate E_1 and E_2 at 573 K.

The time factor values were established for aluminium as the thermally stable sample, over the temperature range 563 – 583 K at a heating rate of 0.06 degree/sec.

Results and discussion

The recorded DTA curve of the catalyst, the calibration curve plotted as the time factor against time, and the calculated momentary values of the heat flux from the sample during the reduction run, as the curve dQ/dt *vs.* time, are shown in Figs 3a, 3b and 3c, respectively. It can be observed that, on flowing into the DTA cell, hydrogen reacts with the catalyst and essential changes at once occur in the calorimetric sensitivity.

The total heat emitted during the reaction, $Q_r = \int \frac{dQ}{dt}\,dt$, is equal to the area under the curve in Fig. 3c. In the reported example, $Q_r = 1455$ J is obtained. However, if the calorimetric sensitivity changes are not taken into consideration, and the amount of heat is calculated directly on the basis of the DTA curve, the following results are obtained: $Q_r' = 936$ J and $Q_r'' = 3014$ J when $E_1 = 13.6$ μV/mW and $E_2 = 4.5$ μV/mW, respectively are taken as E. High differences between the Q_r', Q_r'' and Q_r values indicate that it is imperative to include the calorimetric sensitivity changes in calorimetric calculations if they are simultaneous with an examined reaction.

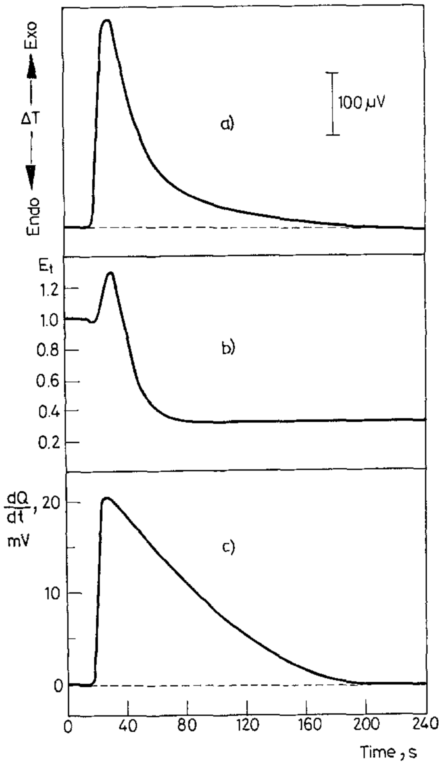

Fig. 3. Reduction run of nickel catalyst at 573 K (the example)
a — DTA curve recorded
b — calibration curve
c — heat flux dQ/dt *vs.* time *t*

A complicated shape of the real calibration curve (E_t *vs.* t) may be due to changes in gas mixture thermal properties and/or to apparatus behaviour (predominantly dissymmetries in the DTA cell). Consequently, the computation of calorimetric sensitivity values as a function of gas mixture composition during gas exchange is a significant problem. The suggested experimental method of calibration should then be used. This procedure may be employed if a high reproducibility of gas exchange operation is warranted.

References

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RÉSUMÉ — L'article décrit une méthode pour déterminer, par voie d'expérience, les valeurs momentanées de la sensibilité calorimétrique de l'analyseur thermique, lorsque la nature du gaz est changée dans la cellule d'ATD.

ZUSAMMENFASSUNG — Der Artikel beschreibt einen Weg zu experimentellen Bestimmung augenblicklicher Werte der Kalorimeterempfindlichkeit des Thermoanalysators bei Austausch der Art des Gases in der DTA-Zelle.

Резюме — Настоящая статья описывает способ экспериментального определения мгновенных значений калориметрической чувствительности термического анализатора, когда тип газа в ячейке ДТА меняется.