Journal of Thermal Analysis, Vol. 47 (1996) 445-452

MEASUREMENT OF HETEROGENEOUSLY CATALYZED GAS REACTIONS BY DSC

G. Hakvoort

Delft University of Technology, Chemistry Department, Julianalaan 136, 2628 BL Delft
The Netherlands

Abstract

Gas reactions, catalyzed by solid catalysts, can be measured by DSC. In the experimental set-up an open sample pan with catalyst (powder or pellet) is placed on the sample side of the DSC sensor. The reactive gas mixture flows through the cell and reacts on the catalyst surface. The heat effect, caused by this reaction, results into a DSC signal.

The calibration procedure is described for quantitative evaluation of the DSC measurements. For illustration four different reaction systems are discussed.

Keywords: catalysts, catalyst activity, catalyst deactivation, DSC, gas reactions, kinetics

Introduction

Normally DSC is used for measuring heat effects of solid or liquid samples, contained in a sample pan. The heat is produced by physical or chemical reactions of the sample, for instance melting or oxidation, and measured by the DSC sensor. In case of reactions between flowing gases, DSC measurement seems impossible, because the reaction will proceed in the whole DSC cell, and not only at the sample side of the DSC sensor. However, when the reaction does not proceed as a homogeneous reaction in the gas phase, but only proceeds at a solid or liquid catalyst, DSC measurement is possible. Then the catalyst is contained in an open sample pan and placed on the sample side of the DSC sensor. The heat, produced at the catalyst, can be detected by the sensor. For a quantitative evaluation the calibration problem must be solved.

This kind of DSC measurement can be performed for a lot of reactant/product systems, provided that the DSC cell is not injured by the gases or the catalyst and that the produced heat effect is within a reasonable range. Further condensation of reactants or products in the instrument should be avoided. In this contribution four systems are discussed: the formation of methane from $CO+H_2$ over a nickel catalyst [1, 2], the high pressure reaction of $CO+H_2$ into methanol over a copper catalyst [3], the decomposition of methanol into $CO+H_2$ at normal pressure [4], and the selective catalytic reduction (SCR) of

0368–4466/96/ $ 5.00

John Wiley & Sons, Limited
Chichester

NO with NH_3+O_2 over a V_2O_5 containing catalyst [5, 6]. In all systems a quantitative evaluation of the DSC signal will be possible after calibration.

Upset and calibration

On the hand of the methane formation reaction [1, 2] the technique will be discussed. The concerning reaction is strongly exothermic:

$$CO+3H_2 \rightarrow CH_4+H_2O;\ \Delta H = -217\ \text{kJ mol}^{-1}\ CO \tag{1}$$

At temperatures lower than 723 K this reaction does not proceed as homogeneous gas phase reaction, but can only be performed on a catalyst. The applied catalyst is Ni/Al_2O_3. A pellet or an amount of 1–10 mg powdered catalyst is placed in an open DSC pan on the sample side of the DSC sensor. Reference material is pure Al_2O_3 (pellet or powder). The kinetic experiment consists of three heating steps:

- Firstly the catalyst must be reduced, since a part of the nickel is oxidized into NiO by contact with air. Therefore a run is made in pure H_2 from 300–673 K with a heating rate of 20 K min^{-1}.
- After cooling down a baseline is measured, also in pure H_2, from 373–673 K, with a heating rate of 10 or 20 K min^{-1}
- After cooling down unto 373 K the hydrogen flow is changed into a mixture of H_2+x % CO, x being 0–2%. Now an exothermic effect is visible, caused by the adsorption of CO on the catalyst surface.

When the adsorption is complete, and the DSC signal is back to the baseline, a heating run is started from 373–673 K, with 10 or 20 K min^{-1} (reaction line). Now from some temperature an increasing exothermic effect becomes visible, caused by the methanation reaction (Fig. 1). The difference Δ between baseline and reaction line increases until a nearly constant value at high temperature, where all the CO arriving at the catalyst surface, reacts immediately.

The calibration of the DSC signal cannot be performed with the normal procedure: melting of indium in a closed pan in the adequate gas phase. The reason is that the experiment is performed in an open pan. From the heat evolved at the catalyst sample, a part flows to the DSC sensor, resulting into the DSC signal Δ, and a part flows directly into the surrounding gas phase. The fraction of heat, flowing to the sensor depends on the thermal properties of the sample (dimensions, thermal conductivity) and of the gas phase (specific heat).

This effect is illustrated in Fig. 1, where a pellet (17.22 mg) and a powder (1.22 mg) are measured: although at high temperature the reaction rate on the pellet is higher, the DSC signal Δ is lower than for the powder.

There are three possible ways of calibration:

1. Firstly, the in- and outgoing gases are to be analyzed by GC or MS. Now the reaction rate r (moles CO, reacting per second) can be determined. The corresponding heat effect is $Q' = r \times (\Delta H)$, (ΔH) being 217 kJ mol^{-1} CO. Now the calibration factor (C.F.) can be calculated according to:

$$\Delta \times (\mathrm{C.F.}) = r \times (\Delta H) \tag{2}$$

The value of (C.F.) has been determined for several experiments [2] and happens to be constant between 473–673 K, for the DuPont 910 DCS cell.

2. A second possibility is the melting of a metal (tin or indium), placed on top of the sample in a gas mixture with thermal properties, corresponding to the reaction gas mixture. The values of (C.F.), determined with both methods agree very well [4].

3. A third method of calibration (internal calibration) can be applied, when the reaction at high temperature proceeds to completion [2].

In Fig. 1B the Arrhenius plot is given for the reaction on a catalyst pellet.

At low temperature the reaction is determined by the chemical catalyst activity, showing a high activation energy. At high temperature the reaction is so fast, that all the CO, arriving at the catalyst, reacts immediately. It must be realized that the nearly constant rate at high temperature does not correspond to the reaction of all the CO in the inlet gas flow. Only the fraction that in the given residence time arrives to the external catalyst surface, will react. This fraction ξ depends on geometrical factors (volume of the DSC cell, shape and dimensions of the sample) and the flow conditions, but not on the activity of the catalyst sample (being high enough). At standard conditions, with a few mg of catalyst powder in a pan with a diameter of 6 mm, the value of $\xi = 65.3\%$ at

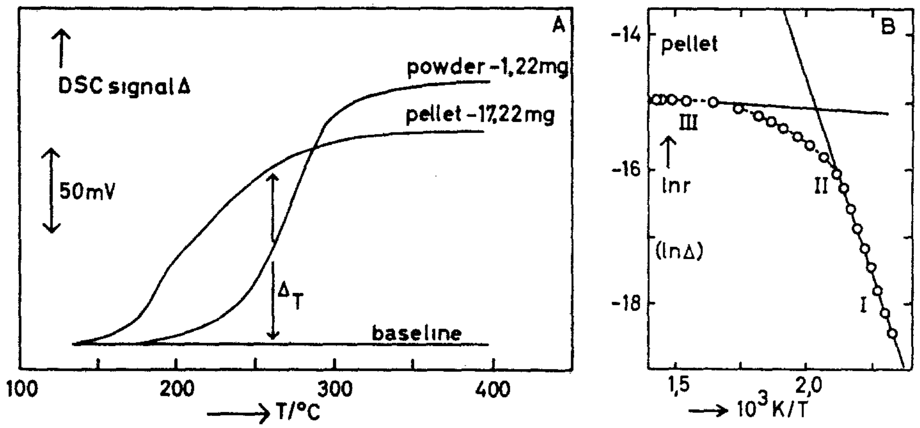

Fig. 1 A. DSC plot of the reaction of CO $+H_2$ into CH_4 over a Ni/Al_2O_3 catalyst (pellet and powder). B. Arrhenius plot, constructed from the DSC experiment with the catalyst pellet [2]

668 K. For pellets somewhat different values are found, depending on the value of the external contact area with the gas phase [2]. Now, at standard conditions, the reaction rate is known at 668 K, so the value of (C.F.) can be calculated from the DSC signal Δ.

Application

With the described DSC procedure a fast and reliable method is available for testing of catalysts and catalytic reactions. So, the standard activity (mol CO g cat^{-1} h^{-1}) can be determined, from the low temperature region of the Arrhenius plot, at 513 K [1, 2]. Further, the rate of catalyst deactivation can be measured from successive reaction runs with the same catalyst sample. These data are important for finding a stable and active catalyst. From experiments in different CO and H_2 concentrations the kinetics of the catalytic process can be determined [1].

Also different gas reactions are investigated by DSC. The exothermic reaction of $CO+H_2$ into methanol on a $Cu/ZnO/Al_2O_3$ catalyst can be performed in a high pressure DSC at 40 bar [3], according to:

$$CO+2H_2 \rightarrow CH_3OH;\ \Delta H = -100\ \text{kJ mol}^{-1}\ \text{CO} \tag{3}$$

The reaction is performed in a gas mixture containing H_2+9.82% CO+0.70% CO_2, at a total flowrate of 1.5 l h^{-1} (measured at 273 K and 1.10^5 Pa). The baseline is measured in a gas consisting of H_2+10% N_2. On account of the equilibrium conditions, the application of a high pressure is necessary.

In Fig. 2 a DSC experiment is shown. In this figure three regions are visible: I. at low temperature an increasing rate. From this region the standard activity can be calculated and compared with figures, obtained by flow reactor measurements [3]. A region II is visible with decreasing rate, caused by the shift of the equilibrium to lower methanol concentrations at increasing temperatures. In region III the DSC signal Δ is increasing again. This could be explained by the conversion of methanol into dimethylether at these high temperatures, according to:

$$2CH_3OH \rightarrow CH_3OCH_3+H_2O \tag{4}$$

Further also side reactions, like the formation of methane, become possible at these high temperatures. Calibration can be performed with the first two methods, but not with the internal calibration method, since not all the CO arriving at the catalyst reacts into methanol at high temperatures, caused by the shift of the equilibrium and the occurrence of side reactions. In spite of these problems, the testing of catalysts in a HP-DSC can be easily performed (within

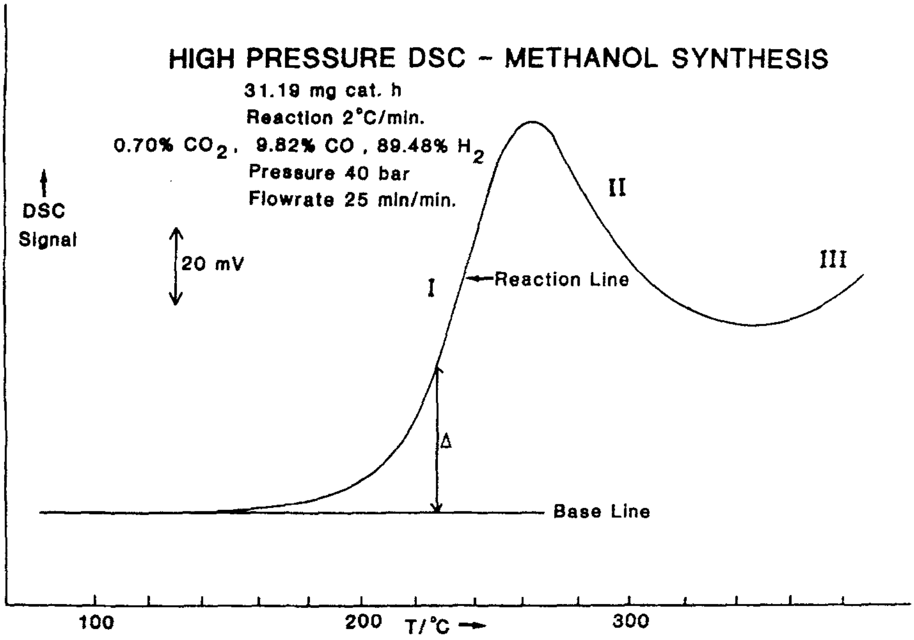

Fig. 2 HP-DSC plot of the reaction of $CO+H_2$ into CH_3OH at 40 bar ($4\cdot10^6$ Pa) over a $Cu/ZnO/Al_2O_3$ catalyst powder [3]

a few hours per experiment) and is much faster than the measurements with pressurized flow reactors. For the testing of the activity of catalysts, however, also the reverse reaction could be applied [4]. Now the DSC experiment can be performed at normal pressure, using a mixture of N_2 with 3.48% methanol (flowrate 1.05 l h^{-1}, measured at 273 K and 1.10^5 Pa). The baseline is measured in pure N_2. The DSC plot is given in Fig. 3. Although the decomposition reaction proceeds to completion, the internal calibration method cannot be used, because of a side reaction: the DSC curve shows an increasing rate with temperature in the lower temperature region, but the absolute value of the signal Δ decreases at higher temperatures, caused by the occurrence of the exothermic formation of methane at high temperatures. This method, DSC measurement of the decomposition of methanol, is very useful for a first testing of catalysts for the production of methanol, but is more easily and much faster to perform than the catalytic experiments in the HP-DSC.

A fourth reaction that has been investigated in literature [5, 6] is the so-called selective catalytic reduction (SCR) of NO with NH_3+O_2 over a V_2O_5 containing catalyst, according to the reaction:

$$4NO+4NH_3+O_2 \rightarrow 4N_2+6H_2O \qquad (5)$$

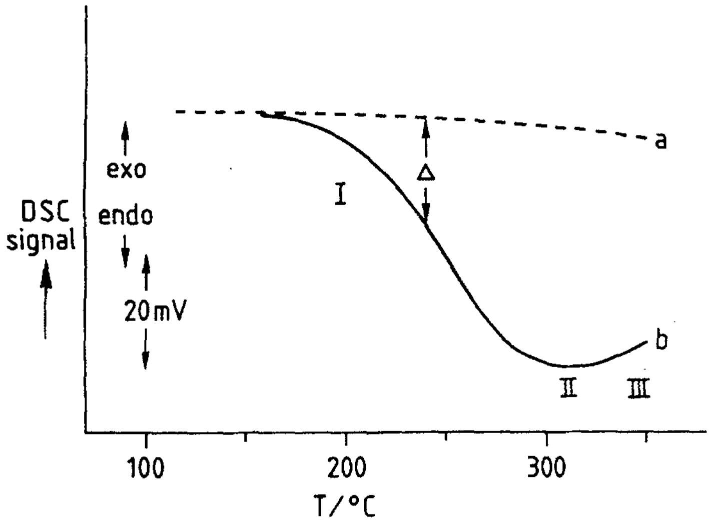

Fig. 3 DSC-plot (at normal pressure) of the decomposition of methanol into CO + H_2 over 4.41 mg of Cu/ZnO/Al_2O_3 catalyst powder [4]

The reaction is exothermic with a heat effect ΔH = –1625 kJ/4 moles NO. Unfortunately, a lot of side reactions are possible, so that in most cases DSC measurements alone are not sufficient for investigation of this reaction. Only with a very selective catalyst, $V_2O_5/TiO_2/SiO_2$, separate DSC measurements are sufficient. This is shown in Fig. 4, where the DSC curve is given, together with the concentrations of the different compounds, measured by MS (mass spectrometry). The decrease of the NO and NH_3 concentrations and the increase of the N_2 and H_2O concentrations correspond to Eq. (5). Now the rate could be calculated from the DSC curve, since only one reaction is concerned, with a definite reaction heat per mole NO.

Conclusions

Reactions between gases can be measured by DSC, provided that they only proceed on a solid (or liquid) catalyst. This catalyst is contained in an open sample pan and placed on the sample side of the DSC sensor.

Calibration of the DSC signal can be performed in several ways.

1. By melting of a piece of metal (In, Sn) on top of the catalyst sample, in a gas phase with identical thermal properties as the reaction gas.
2. By measurement of the in- and outlet gas concentrations with MS or GC.
3. By internal calibration when the reaction proceeds to completion and becomes very fast at high temperatures.

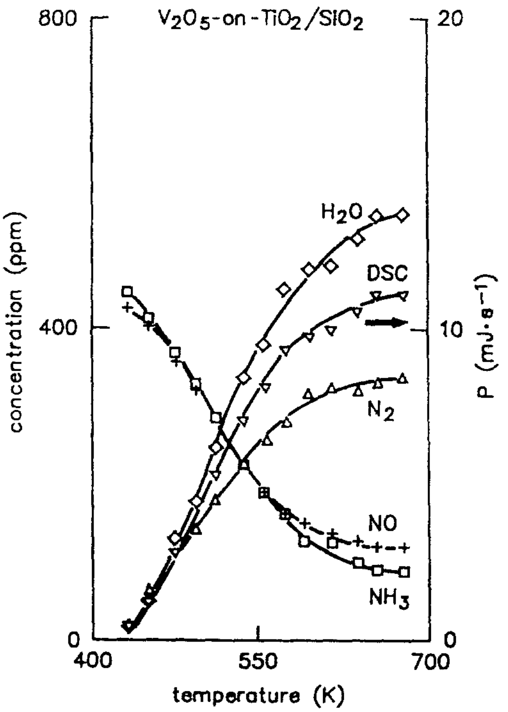

Fig. 4 Plot of the selective catalytic reduction of NO with NH_3+O_2, over a V_2O_5 on TiO_2/SiO_2 catalyst. The reaction is performed in the Setaram DSC 111. The DSC plot is given and also the concentrations of NO, NH_3, N_2 and H_2O as a function of the temperature, measured by mass spectrometry [5, 6]

Method 3 can only be applied for the formation of methane. The other reaction systems discussed in this contribution show side reactions or do not go to completion for equilibrium reasons.

The exothermic formation of methanol can be investigated with a HP-DSC at 40 bar.

Similar results concerning the standard activity and deactivation behaviour of methanol formation catalysts, can be obtained by the investigation of the reverse reaction (decomposition of methanol into $CO+H_2$) in a normal pressure DSC.

DSC measurements also have been applied in the selective catalytic reduction of NO with NH_3+O_2. Since a lot of side reactions are possible, DSC meas- urements are only useful when a really selective catalyst is used.

The DSC measurements can be used for the determination of absolute and relative catalyst activities, catalyst deactivation, activation energies and kinetics of the catalyzed gas reactions.

Other heterogeneously catalyzed gas reactions also could be measured by DSC, provided that the reactants, products and catalysts are not aggressive for the cell, and no condensation proceeds, at least in the inlet gas flow.

Compared to other methods (flow reactor measurements with gas analysis), the DSC method provides a fast way for selection of catalysts. After appropriate calibration, also quantitative evaluation of the catalyst activities can be performed.

References

1 G. Hakvoort and L. L. van Reijen, Thermal Analysis, Proc. 7th ICTA, Vol. 2, ed. B. Miller, Wiley 1982 p.1175.
2 G. Hakvoort, W. van der Klugt, Y. Timmerman and L. L. van Reijen, Thermochim. Acta, 85 (1985) 319.
3 G. Hakvoort, J. Thermal Anal., 33 (1988) 1235.
4 G. Hakvoort and Xu Xiaoding, J. Thermal Anal., 37 (1991) 1269.
5 J. J. P. Biermann, H. den Daas and F. J. J. G. Janssen, Thermochim. Acta, 133 (1988) 169.
6 J. J. P. Biermann, "The Behaviour of ammonia in the selective catalytic reduction of NO and in the selective oxidation by oxygen", Thesis, Enschede 1990, ISBN 90-353-1025-X.