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THE USE OF A HEAT-FLOW DIFFERENTIAL SCANNING CALORIMETER AS A PLUG-FLOW FIXED-BED REACTOR IN HETEROGENEOUS CATALYSIS

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ABSTRACT

Some aspects of the use of a heat-flow differential scanning calorimeter for studying catalysts are described in this study. The DSC is coupled to a mass spectrometer in order to analyse the gas mixture that leaves the catalyst bed in the DSC reactor. DSC is a physical means of analysis: it does not disturb the reaction. Attention is focused on the calibration of the DSC with a probe on the basis of the so-called Joule effect. The calibration is carried out over a large temperature range of 300–700 K both in the absence of flow and under flow conditions.

INTRODUCTION

The performance of catalysts for the selective catalytic reduction (SCR) of NO with NH_3 and O_2, producing N_2 and H_2O is usually evaluated through the analysis of the reactants and products with the aid of chemiluminescence, gas chromatography and/or mass spectrometry [1]. As the SCR reaction is highly exothermal ($\Delta H = -407.7$ kJ mol^{-1} of N_2 formed), it may also be evaluated by differential scanning calorimetry (DSC) [2]. The output signal of the DSC is directly proportional to the heat produced in the catalyst bed.

The design of the sample holders of the DSC used in this study is comparable with that of a conventional plug-flow fixed-bed reactor. The reactants and products were analysed on-line by means of a sector mass spectrometer.

To study the kinetics of reactions over catalysts, it is necessary to vary experimental parameters such as the amount of catalyst, concentration of reactants, flow through the catalyst bed and the temperature of the bed. The question is: what is the effect of these variations on the performance of the DSC. The amount of catalyst is limited by the sensor volume. The low concentration of the reactants and of the products used in this study does

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not influence the thermal conductivity of the gas mixture. As far as we know, no data are yet available on the influence of flow and heating rate on the performance of the calorimeter used in this study. In this paper the suitability and reliability of a heat-flow DSC for flow experiments is described. Special attention is given to the calibration procedures of the DSC and the effects of the gas flow and heating rate on it. We compared the static calibration performed with indium and the dynamic calibration carried out with the aid of a probe that was developed in our laboratories.

EXPERIMENTAL

A Setaram Tian Calvet microcalorimeter of the twin-conduction type (DSC 111G) was used. A more detailed description of the DSC is given by Marano [3].

The reaction system used, which is shown in Fig. 1, consists of a gas-mixing system, a differential scanning calorimeter and a mass spectrometer. Both the sample and the reference reactor were used in downstream mode. It appeared that a different flow path of helium, viz. the reference reactor in upstream mode and the sample reactor in downstream mode, did not affect the amount of heat measured. The heat-flow DSC was coupled via a leak valve to a mass spectrometer for gas-composition analysis [1]. All tubing located between the DSC and the mass spectrometer was kept at 120–140 °C in order to avoid adsorption and/or condensation of the various gaseous compounds on the wall of the tubing.

Quartz tubes were used as reactors for the catalyst and the reference material. The reactors of our own construction were 15 cm in length with an external diameter of 6.8 mm and an internal diameter of 5 mm. Swagelock 1/4 inch connectors with PTFE ferrules were used because of leakage in the connectors that had been purchased from Setaram.

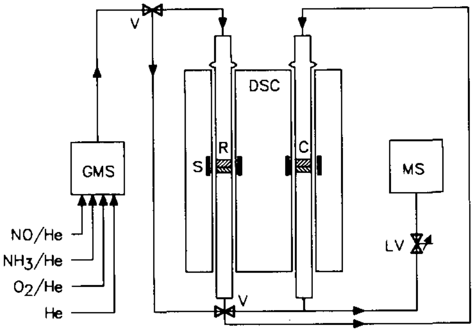

Fig. 1. Apparatus used: C, catalyst; GMS, gas-mixing system; DSC, differential scanning calorimeter; LV, leak valve; MS, mass spectrometer; R, reference; S, sensor; V, valve.

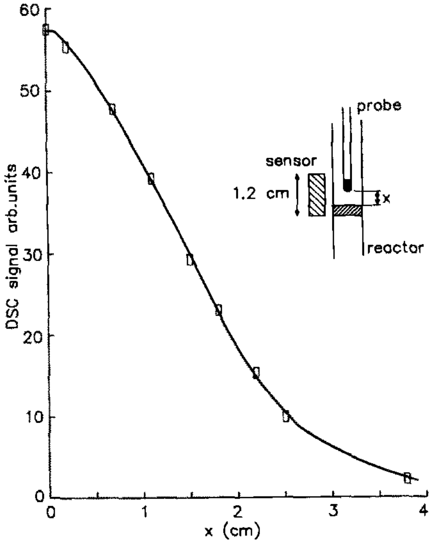

Fig. 2. The distance x of the tip of the probe to the frit of the reactor (no helium flow).

Both the sample and the reference reactor contained a quartz frit mounted just above the lowest point of the measuring zone of the DSC sensor. To achieve this, the diameter of the quartz reactors just outside the oven was enlarged somewhat at about 8 cm above the quartz frit (Fig. 1). The axial length of the DSC sensors is 12 mm. The rate of flow through the reactors was varied from 0 to 200 cm^3 min^{-1}.

The DSC was calibrated using a method based on the so-called Joule effect in the presence and in the absence of reactors. In the absence of reactors the DSC was calibrated by means of the commercial probe supplied with the instrument. However, this probe did not fit into the reactors. Therefore, we developed a probe which fitted the reactors. In this way the calibration procedure could be carried out using gas flow. The probe contains a Canthal wire (100 Ω) which dissipates a fixed amount of energy to the DSC sensor. The wire (length 0.3 m) was wrapped around a quartz pipe (outer diameter 2 mm) and embedded in a ceramic paste. The wire was connected to the power source of the DSC with platinum wires of negligible resistance. The length and the diameter of the probe were 10 mm and 3.5 mm, respectively. The position of the tip of the calibration probe is critical as is the height of the catalyst bed. Figure 2 shows the dependence of the DSC output signal on the position of the probe (x). In this study the maximum height of the catalyst bed in the reactor was 10 mm. During catalytic studies the sample reactor contained the catalyst and the reference reactor contained an appropriate amount of quartz powder in order to minimize the difference in heat capacity between the sample and the reference.

The temperature scale for various heating rates was calibrated by measuring the melting point of indium at various heating rates. The effect of the gas flow through the reactor on the heat of fusion of indium was also determined.

Several reactors were used in order to study the effect of the differences in physical parameters of the reactors (the thickness of the wall, porosity of the quartz frit and the location of the frit and differences in heat conductivity). The reactors are designated in the text by A, B, C, etc. A–B means that reactors A and B are in the sample and reference compartment, respectively.

RESULTS

The effect of gas flow and of the types of reactors on the baseline signal in the low-temperature range is shown in Fig. 3. In the absence of reactors in the DSC the deviation of the baseline was about 0.2 μV K^{-1}, which corresponds to 1.45 μW K^{-1}. The presence of a sample and reference reactor results in different baselines. The calibration of the DSC with indium and with our probe and the effect of gas-flow and heating rate on the calibration will be described later.

Figure 4 shows the effect of the heating rate on the measured melting point of indium. Strong deviations of the melting point of indium (429.76 K)

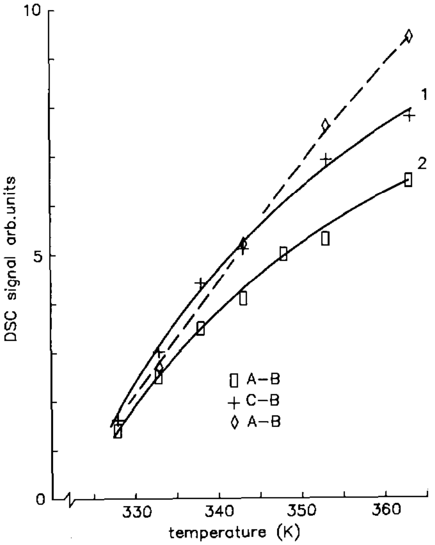

Fig. 3. DSC output signal as a function of temperature for blank experiments. In all experiments the same reference reactor was used. Curves 1 (A–B) and 2 (C–B) were obtained using different sample reactors and no gas flow at $dT/dt = 0$. The dotted line was obtained by performing an experiment with the same set of reactors as used in experiment 1 (curve 1), but with a gas flow of 100 cm^3 min^{-1}.

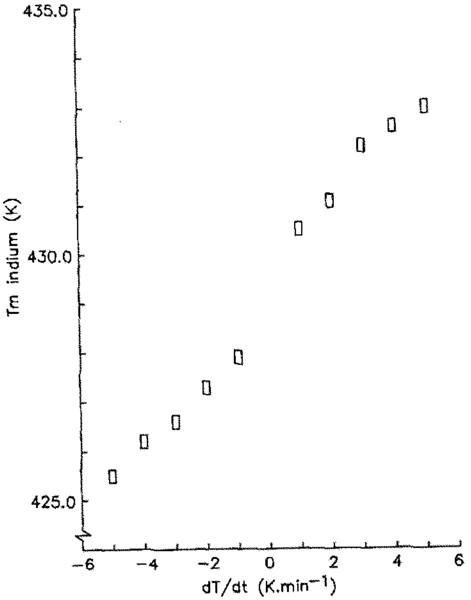

Fig. 4. The apparent melting point of indium as a function of a positive and a negative heating rate.

occur at higher heating or cooling rates. However, it was found that the heat of fusion was independent of the heating or cooling rate, but that it was dependent on the magnitude of the helium flow through the reactor and on

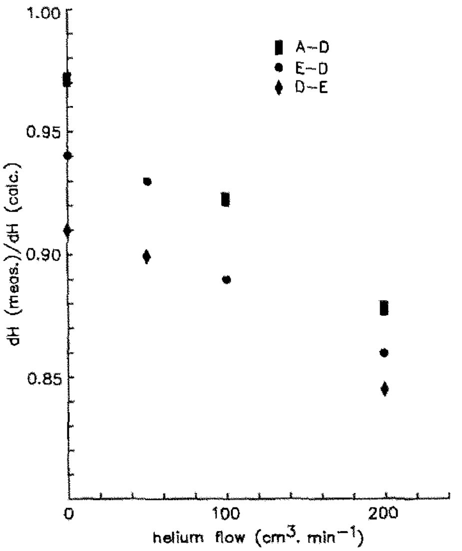

Fig. 5. Relative apparent heat of fusion of indium versus the gas flow for three pairs of reactors. $dT/dt = 2$ K min^{-1}; $\Delta H = 204.66$ mJ.

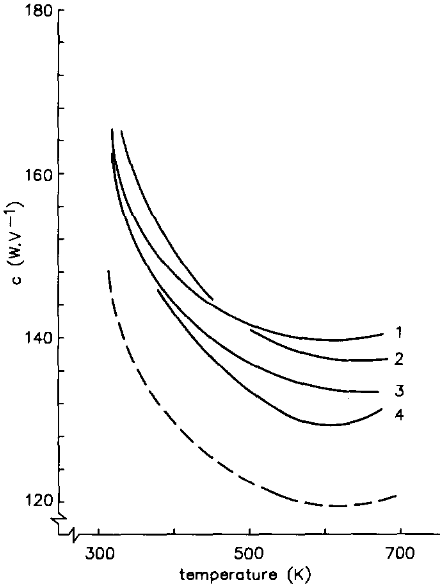

Fig. 6. The calibration constant, c, as a function of temperature in the absence of a gas flow (1; C–F) and in the presence of a helium flow ranging from 25 to 200 cm^3 min^{-1} (2; C–F, 3; G–F). Curve 4 was obtained by means of an experiment in which grains of silica were present in both reactors. The dotted line is the calibration curve in the absence of sample and reference reactors and was obtained using the Setaram probe.

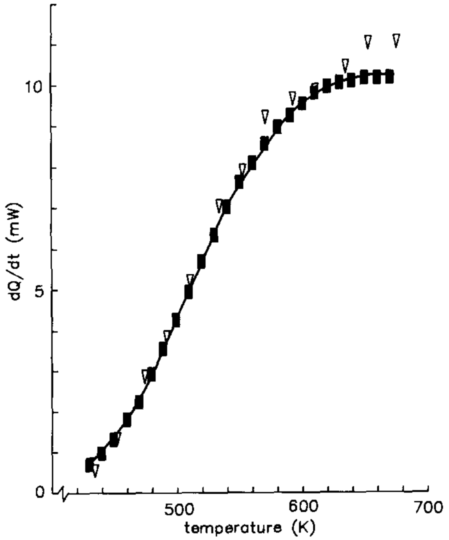

Fig. 7. The heat produced by the reaction of NO, NH_3 and O_2 over V_2O_5 on a TiO_2/SiO_2 catalyst as a function of temperature. The heat measured by the DSC is compared with the heat calculated (▿, triangles) from the reactants and reaction products as measured by mass spectrometry. $[NO_i = [NH_3]_i = 500$ ppm; 2% O_2; flow 100 cm^3 min^{-1}; amount of catalyst 50 mg.

the reactor used, as shown in Fig. 5. The values shown in Fig. 5 are average values obtained from the heating and cooling experiments. Changing the reactors of the sample and reference compartment also resulted in different behaviour with respect to the flow dependency.

The dependence on temperature of the calibration constant, the ratio of the heat production by the probe and the response measured by the DSC, was obtained after calibrating the DSC and can be described as a fourth-power law.

Figure 6 shows several plots of the calibration constant, *c*, versus the temperature. The experimental error in *c* was about 3%. There is a remarkable difference between the curve obtained using an "empty" DSC (dotted line) and the Setaram probe, and the curve obtained using a reference and sample reactor (curves 1 and 2) and our probe. Curve 3 was obtained when gas flows ranging from 25 to 200 cm^3 min^{-1} were used. The presence of silica around the probe during the measurement with a gas flow of 100 cm^3 min^{-1} resulted in curve 4. Again it was found that the use of different reactors gave different results.

Figure 7 shows the heat evolved during the reaction of NO, NH_3 and O_2 over the V_2O_5 on TiO_2/SiO_2 catalyst as a function of temperature. The triangles represent data calculated from the composition of the gas mixture leaving the catalyst as measured with the mass spectrometer.

DISCUSSION

In a recent paper [4] we described the use of a DSC for the determination of the heat evolved at SCR catalysts during the SCR reaction. The DSC technique proved to be highly suitable if the reaction over the catalyst is very selective or if the selectivity of the reaction is known. Selectivity means that the heat measured by the DSC can be attributed to known reactions. The heating rate showed some influence on the relationship of the heat evolved and on the temperature.

The symmetry of the DSC is of great importance when heat production of less than 2 mW must be determined over large temperature intervals and using high heating rates. This is because the difference in heat capacity of the reactors used can result in heat effects of about 7 mW. In order to avoid these large differences in heat produced, the sample and reference reactor should be almost identical with respect to their heat-transfer coefficients.

The dynamic calibration procedure based on the Joule effect is reproducible with an accuracy of better than 3% at heating rates up to 10 K min^{-1}. The procedure can be used for the temperature range 300–873 K. The difference in sensitivity (defined as $1/c$) of a DSC equipped with and without reactors is about 15%; curves 1 and 2 versus the dotted line in Fig. 6, assuming that our probe is comparable with the commercial probe. Gas flow improves the sensitivity ($1/c$) of the instrument by about 4% (Fig. 6, curves 1 and 2) and the heat yield is decreased at higher flow rates (Fig. 5). Flows varying from 25 to 200 cm^3 min^{-1} do not influence the curve of the calibration constant versus temperature using our probe (curve 3 in Fig. 6). However, as can be seen in Fig. 5, the relative heat depends on the flow in case of using static calibration with indium. This can be ascribed to the worse contact of the small amount of indium in the reactor which causes incomplete heat transport. From Fig. 4 it follows that the temperature scale during a run needs correction as a result of the heating rate. The heating rate to be used depends on the time needed to obtain steady-state conditions at the catalyst. If the rate of reaction is too low, it is necessary to measure the activity as a function of temperature under isothermal conditions. From the experiments described below it can be concluded that 2 K min^{-1} is an acceptable heating rate [4].

The height of the catalyst bed in the sample reactor should not exceed 10 mm (Fig. 2). This means that variations in space velocity between 15000 h^{-1} and 60000 h^{-1} could be achieved by varying the flow from 50 to 200 cm^3 min^{-1}. However, the flow should be kept at around 50 cm^3 min^{-1}, because the sensitivity of the DSC decreases with increasing gas flow (Fig. 5). Varying the amount of catalyst (10–100 mg) results in space velocities in the range 15000–150000 h^{-1} at 50 cm^3 min^{-1} using particles with diameters ranging from 0.25 to 0.50 mm. The calculated ratio of the rates of heat transfer in the radial and axial directions is about 3.8, which means that about 26% of the heat evolved is not detected. However, from our measurements (Fig. 5) it follows that in the absence of a helium flow, and even at a high helium flow, heat loss was about 5% and 15%, respectively. Figure 6 suggests that the bulk of the energy transport will occur through the solid phase. Moreover, from the results shown in Fig. 6 it can be concluded that the heat conductivity through the solid is enhanced using a flow and quartz particles around the probe.

The data points calculated on the basis of mass-spectrometry measurements are close to the curve found by means of the measurements with the DSC. The accuracy for the DSC and the MS was 5% and 10%, respectively. The S-curve shown in Fig. 7 suggests that no hot spots are present in the catalyst bed during the reaction at each temperature. The heat transfer to the sensor can be improved by using nitrogen instead of helium as the carrier gas. However, N_2 is one of the products of the reaction of NO, NH_3 and O_2 and thus cannot be detected if N_2 is used as the carrier.

CONCLUSION

The plug-flow fixed-bed differential scanning calorimeter is a versatile instrument in studying SCR catalysts. The presence of reactors in the DSC, the use of gas flow through the reactors and the presence of solids in the reactors influence the calibration curve slightly. When a new pair of tubes is introduced in the calorimeter, the instrument must be calibrated again. Space velocities ranging from 15 000 h^{-1} to 150 000 h^{-1} can be applied. The heat yield during the reaction of NO, NH_3 and O_2 is higher than 90% and depends on the extent of the gas flow. The heat transfer during the static calibration (indium) is flow dependent, whereas in the dynamic calibration it is not. The calibration probe based on the Joule effect was developed in our laboratories and appeared to be an excellent probe for calibrating the DSC under flow conditions.

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