THE USE OF DSC TO STUDY THE SELECTIVE
CATALYTIC REDUCTION OF NO WITH NH3

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ABSTRACT

Differential scanning calorimetry (DSC) has the advantage that it allows the chemical reaction rate to be followed at temperature–programmed conditions. In complicated reactions, such as the reaction of NO and NH3 over a catalyst, it is unwise to employ the heat of the overall reaction as a measure of the extent of the reduction of NO. Therefore, these measurements are accompanied by mass spectrometric analysis in order to measure the activity and selectivity of the reaction.

This paper presents the results of the effect the heating rate has on the performance of a selective V_2O_5 on TiO_2/SiO_2 catalyst. Moreover, typical results of the reaction of NO, NH3 and O_2 over samples of a non–selective catalyst (CuO on SiO_2) and a selective catalyst (V_2O_5 on TiO_2/SiO_2) are presented.

INTRODUCTION

Differential Scanning Calorimetry (DSC) is a suitable technique to study the kinetics of heterogeneous catalytic reactions. The signal of the DSC is proportional to the heat production, provided that the reaction heat is independent of the temperature. Proportionality of the signal to the reaction rate of one particular reaction however, requires a catalyst showing a selectivity of 100%. That is probably one of the reasons that most DSC studies in catalysis concern the methanation reaction over nickel catalysts [1,2,3,4]. DSC has also been used to study the reaction of NO and NH3 [5]. The instruments used in those studies have permanently open (aluminium) cells, placed on the sensors. The catalysts are placed in the sample cell and exposed to the reactants. In this study however, the DSC sensor is placed around a conventional fixed bed reactor.

The usefulness of instrument and method for the study of the kinetics of a reaction are illustrated with the selective catalytic reduction (SCR) of nitric oxide with ammonia. The most important and desired overall reaction in the SCR of NO with NH3 is:

$$4 NO + 4 NH_3 + O_2 = 4 N_2 + 6 H_2O + 1631 \text{ kJ.mol}^{-1} \qquad (1)$$
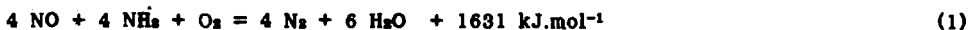
However, side reactions such as: the oxidation of ammonia with oxygen to nitric oxide,

nitrous oxide and nitrogen; and the reduction of nitric oxide with ammonia to nitrous oxide [6,7] are also possible. These reactions have substantially lower reaction heats. Therefore, a change of selectivity (or activity) may be easily detected. The influence of the scanning rate on the DSC signal was examined using a catalyst showing almost 100% selectivity for reaction 1.

Reaction heat and gas composition were correlated for two catalysts which exhibited different selectivities. Gas composition was determined by means of a mass spectrometer (MS).

EXPERIMENTAL

The Setaram DSC 111-G used is a Tian-Calvet heat-flow calorimeter of the twin-conduction type [8]. The calorimeter consists of a symmetrical, thermostated furnace-block in which two alumina pipes (internal diameter 7 mm) are placed. The heat sensors, consisting of Pt-thermopiles, are situated around the middle of the pipes.

The catalyst was introduced in a quartz pipe (sample cell) with an internal diameter of 5 mm. The reference pipe contained the support of the catalyst (silica). These pipes designated in the text as reactors were placed vertically in the calorimeter.

Figure 1 shows the experimental setup. The reactors were modified in such a way that the catalyst bed was positioned in the sensor region. The direction of the gas flow through the catalyst bed and the reference was always downstream. The reactors were connected in series, with the reference reactor coming first. Gases were analysed with the aid of a Varian Mat 112 mass spectrometer previously described [10].

The DSC was calibrated by means of a method based on the Joule-effect. For this purpose the Setaram probe containing a Pt-wire resistor (100 Ω) and the power source (EJ-1) of the instrument were used. Heat pulses of 100 mW were dissipated during the calibration procedure for 200 s. The time between the pulses was 400 s. The calibration constant was calculated from the areas of the pulses. The disadvantage of this probe is that it does not fit into the reactor. A smaller probe [9] was developed, consisting of a small quartz pipe wrapped by a canthal wire (100 Ω).

The reactor used was calibrated with and without flow, and with different materials in the reactor around the smaller probe.

The catalysts were prepared by means of homogeneous deposition precipitation [11]. The composition of the V_2O_5 on TiO_2/SiO_2 catalyst (A) is 4.5%, 24% and 71.5% (by wt) respectively. The composition of the CuO on SiO_2 catalysts (B) is 30% and 70% respectively. Both catalysts were pelleted, crushed and sieved into the fraction range of 0.25 to 0.50 mm. An equivalent amount of silica was used as reference. The amount of catalyst used in each experiment was 50 mg, which resulted in a catalyst bed of about 5 mm in height. The catalysts were pretreated in situ at 673 K in a 25% O_2 in He flow for one hour.

DSC blanks were obtained using helium with a flow rate of 100 cm³.min⁻¹ Two types of experiment were carried out. First, DSC traces were recorded using heating rates of 0, 1, 2, 4, 6 and 8 K.min⁻¹ at temperatures in the range of 523–573 K. Catalyst A was used because of its high selectivity to N_2 in the SCR reaction. Secondly, the gas composition (MS) and reaction heat (DSC) over two catalysts were measured during a scan of 2 K.min⁻¹ from 423 to 673 K. The analysis of the reaction products was carried out during intervals of 3 minutes. The reaction heats were measured with the aid of the DSC and calculated from the concentrations measured by means of the MS, using the changes in the concentration of NO, NH_3 and H_2O, and their standard heats of formation.
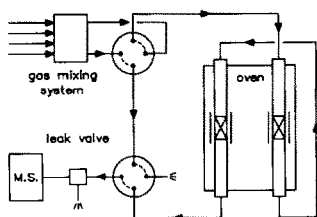

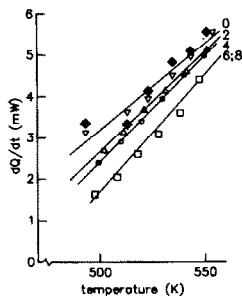Figure 1. Apparatus used for combined DSC/MS measurements

Figure 2. dQ/dt versus T using various heating rates (figures in K.min⁻¹). The solid points were obtained by means of the mass spectrometer. $[NO]_1=[NH_2]_1=$ 500 ppm; $[O_2]_1=$ 2% (vol.), flow 100 cm³.min⁻¹, amount of the V_2O_5 on TiO_2/SiO_2 catalyst 50 mg.

RESULTS

The dependence of the calibration constant c (equation 2) on temperature was examined in the temperature range of 300–823 K.

$$P = c \cdot R \tag{2}$$

in which P is heat production (mW); c is the calibration constant (W/V); and R is the response (mV). Scanning rates lower than 5 K.min⁻¹ and using an 'empty' calorimeter with the probe of Setaram did not influence the constant c. Calibration of the calorimeter by means of the probe developed in the reactor resulted in an 11% higher constant over the total temperature range.

For the reactor used in this study, gas flows up to 200 cm³.min⁻¹ and catalyst grains around the probe gave no significant changes of the constant c. The accuracy of the calibration was 3% over the complete temperature range, and for each scanning rate. This is in accordance with the accuracy mentioned by Calanan et al. [12].

Figures 2 and 3 show the relation of the heat measured by means of DSC and temperature for various scanning rates. In Figure 2 the temperature is corrected for the temperature difference between the furnace and the inner side of the reactors, as observed in melting experiments of indium and zinc. The solid points in Figure 2 show the reaction heat as calculated from the MS-analysis for the experiments which were

carried out at constant temperature. Figure 3 resulted from interpolation of the data of Figure 2.

In Figure 3 it can be seen that there is a linear dependence between heat production (and thus the reaction rate) and scanning rate. The decrease of the heat production in proportion with the scanning rate is probably caused by lack of steady state in the reaction. At scanning rates lower than 4 K.min⁻¹ the difference between the highest and the lowest value for dQ/dt is about 0.3 mW.

Figure 4 shows the relation between the heat calculated from MS data and the heats measured by means of DSC for the two catalysts.
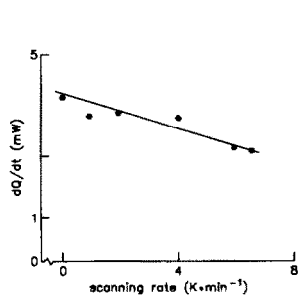

Figure 3. dQ/dt versus scanning rates. dQ/dt values were interpolated from Figure 2. For other conditions see Figure 2.
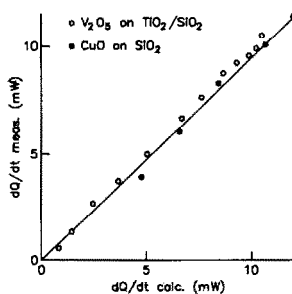
Figure 4. Correlation of dQ/dt obtained from MS data and dQ/dt measured with the aid of the DSC for two catalysts. The straight line is the theoretical relation.
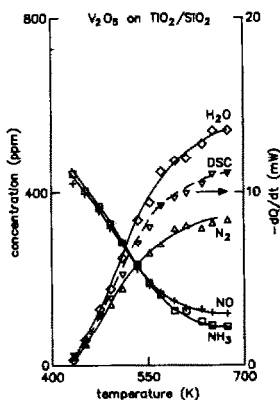

Figure 5. Concentration as a function of temperature over the V₂O₅ on TiO₂/SiO₂ catalyst. The dotted line represents the relation between dQ/dt and T. Scanning rate 2 K.min⁻¹. Other conditions as in Figure 2.

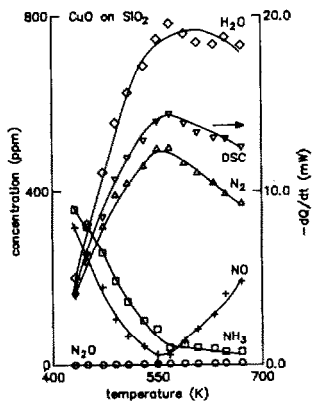Figure 6. Concentration as a function of temperature over the CuO on SiO₂ catalyst. Scanning rate 2 K.min⁻¹. Other conditions as in Figures 2 and 5.

Figures 5 and 6 show the concentration profiles of NO, NH_3, N_2 and H_2O over catalysts A and B respectively. N_2O production was negligible. Mass balances were better than 8%. The dotted lines represent the evolved heat as a function of temperature. Finally, the heats measured over catalyst A are used to plot the Arrhenius curve shown in Figure 7. For this calculation it was assumed that the reaction was approximately first order in nitric oxide, and zero order in ammonia, water and oxygen. The value for k was calculated by means of equation 3.

$$\ln(k) = \ln(-\ln(1-x)) \hspace{4cm} (3)$$

k is the reaction rate constant and x is the conversion equal to the ratio of observed heat and heat at maximum conversion. The apparent activation energy calculated from this plot was 47 kJ.mol^{-1} for the temperature range of 423–673 K.
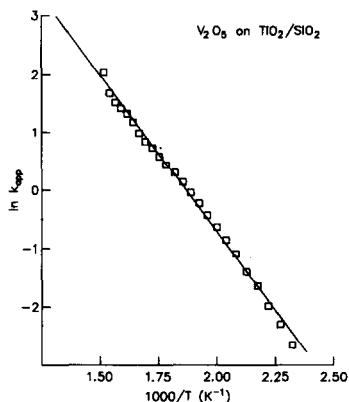

Figure 7. Arrhenius plot of the data obtained from measurements with the V_2O_5 on TiO_2/SiO_2 catalyst. Conditions as in Figure 2.

DISCUSSION

The dynamic calibration procedure is preferable to the use of isothermal calibration with indium. That is to say, the calorimeter can be calibrated over an extended temperature range and, moreover, the instrument is used in the scanning mode more often than in the isothermal mode.

From Figure 4 it follows that heat loss as a result of the use of a catalyst and of the flow is negligible. This means that the heat measured is equal to the reaction heat. The low levels of concentration hardly influence the thermal conductivity of the gas mixture before and after the reaction. The steady state during a run was approximated using scanning rates of 2 K.min^{-1} (Figure 2). This is in contrast with the scanning rates used by Beecroft et al. [1] and Hakvoort et al. [2] of 32 and 10 K.min^{-1} respectively. Generally speaking, using high scanning rates for the 'fixed-bed DSC' introduces a radial temperature gradient over the catalyst bed, which will influence steady state conditions.

It can be inferred from the concentration profiles of NO, NH$_3$ and N$_2$ that NO is produced through the oxidation of NH$_3$ over the CuO on SiO$_2$ catalyst at temperatures in excess of 550 K (Figure 5). The concentration of NO increases and the concentrations of N$_2$ and NH$_3$ decrease. The type or types of the overall reactions occurring during the reduction of NO were found by using labelled molecules such as ^{18}NO and ^{16}NH$_3$ [6,7]. These experiments confirmed that NH$_3$ is oxidised to NO at higher temperatures. Additional evidence for these findings is the fact that the relation between the heat evolved and temperature has about the same form as the concentration profile of N$_2$. The dotted line can be calculated knowing the selectivity of the reaction.

The apparent activation energy of 47 kJ.mol^{-1} occurring in the temperature range of 400–800 K is in agreement with the value of 44 kJ.mol^{-1} (460–500 K) presented in the literature [5].

CONCLUSIONS

Temperature–programmed selective catalytic reduction of nitric oxide with ammonia over various catalysts is useful as a fingerprinting technique. Quantitative data can be obtained if the reaction over the catalyst is selective.

Finally it is emphasized that DSC can be applied in catalysis as a tool for: the determination of reaction kinetics; finding changes in activity and selectivity during the use of a catalyst, i.e. caused by catalyst poisoning or ageing and fast screening of the catalysts.

REFERENCES

[1]   T. Beecroft, A.W. Miller and J.R.H. Ross, J. Catal., 40 (1975) 285.
[2]   G. Hakvoort, W. van der Klugt, Y. Timmerman and L.L. van Reijen, Thermochim. Acta, 85 (1985) 319.
[3]   I.J. Kitchener, N.D. Parkyns and S.B.J. Scott, Anal. Proc., 22 (1985) 237.
[4]   J.R.H. Ross, Anal. Proc., 22 (1985) 239.
[5]   F.J.J.G. Janssen and F.M.G. van den Kerkhof, Kema Sci. Techn. Rep., 3 (1985) 71.
[6]   F.J.J.G. Janssen, F.M.G. van den Kerkhof, H. Bosch and J.R.H. Ross, J. Phys Chem., 91 (1987) 5921.
[7]   F.J.J.G. Janssen, F.M.G. van den Kerkhof, H. Bosch and J.R.H. Ross, J. Phys Chem., 91 (1987) 6633.
[8]   R.T. Marano, Thermochim. Acta, 26 (1978) 27.
[9]   J.J.P. Biermann, P.P. Coelen, H. den Daas and F.J.J.G. Janssen, to be published.
[10] F.J.J.G. Janssen, Thesis, Technical University of Twente, November 1987.
[11] J.W. Geus, In: Preparation of catalysts III, Studies in Surface Science and Catalysis, Scientific bases for the preparation of heterogeneous catalysts. Vol. 16 (1983) 1–33. G. Poncelet, P. Grange and P.A. Jacobs (eds.), Elsevier, Amsterdam.
[12] J.E. Calanan and S.A. Sullivan, Rev. Sci. Instrum., 57 (1986) 2584.