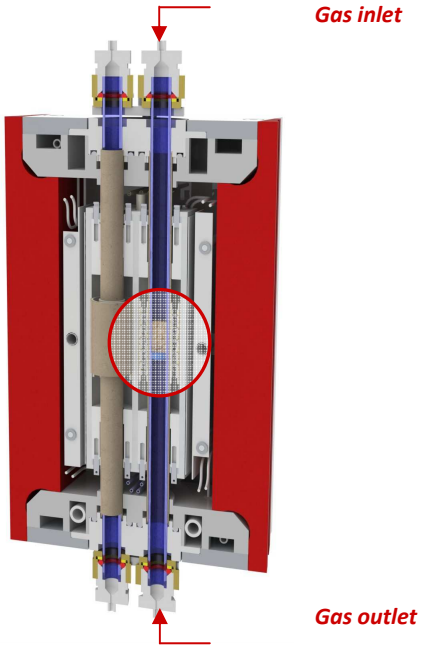
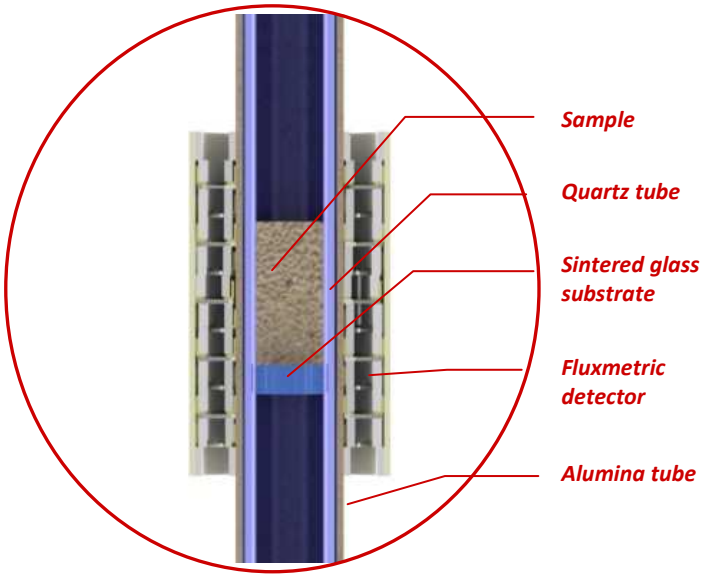
Gas adsorption on catalysts and adsorbents using a quartz tube reactor on a Calvet type DSC

Introduction

The investigation of gas adsorption on catalysts and more generally solid adsorbents requires a very good interaction between the reactive gas and the powder. The Calvet-type DSC offers the main advantage to work with an open tube detection. This configuration 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. The quartz tube reactor is one option for the applications on catalysts, and more generally for all the adsorption investigations. It makes possible the simulation of the use of a plug-flow fixed bed reactor in heterogeneous catalysis.



Calvet type DSC cross section in the vertical mode with the quartz tube reactor



Quartz tube reactor

Experimental

The quartz tube (Figure 1) is introduced in the Calvet type DSC, set in the vertical position (Figure 2). A sintered silica glass frit 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. With such an experimental design, the reactive gas goes through the powdered sample.
The gas can be introduced with a continuous flow, but more generally a gas injection loop is used to produce pulses of known volume of reactive gas. As a quartz tube is used, any type of reactive gas, even corrosive, can be used. The connection with a gas analyzer (GC, MS, FTIR) is very easy to perform.

Results

Such a quartz tube reactor has been used for different applications in the field of catalysis with different EGA combinations. Some examples are given in this application note:

-Heat of adsorption of NH3 on Cu-Beta zeolite

-Reaction of NO, NH3, and 02, over V2O5 on a TiO2/SiO2 catalyst as a function of temperature

-Ammonia adsorption on a sulfonated polystyrene resin-type catalyst (Amberlyst 15)

-Catalytic oxidation of propane

-Interaction of carbon monoxide with zeolites

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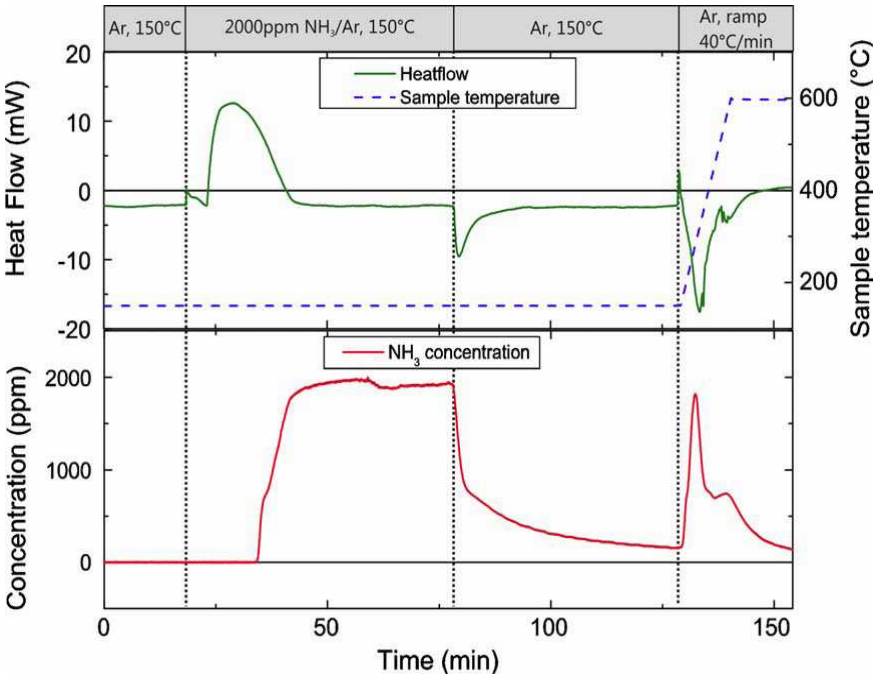

Figure 3 – Thermogram and FTIR signal for an NH3 TPD experiment on a Cu-Beta catalyst

1- Heat of adsorption of NH_3 on Cu-Beta zeolite

The heat of adsorption of NH_3 on Cu-Beta zeolite is investigated at 150°C using the microcalorimeter connected with a FTIR analyzer (Figure 3). Prior to the test, the catalyst was first oxidized by using 8% O_2 at 500°C in order to ensure the removal of all ammonia from the surface. Then, when ammonia was introduced at 150°C, an exotherm is observed corresponding to ammonia adsorption on the zeolite. The FTIR signal also gives an information about the saturation of the catalyst. After the ammonia adsorption phase, the catalyst was exposed to Ar alone. An endotherm was observed due to desorption of loosely bound ammonia, with the corresponding decrease of the NH_3 concentration on the FTIR signal . Then a TDP test was run with a temperature ramp of 40°C/min resulting in a desorption endothermic peak and the corresponding variation of NH3 concentration (FTIR signal).

(N. Wilken, K. Kamasamudram, N. W. Currier, J. Li, A.Yezerets, L. Olsson, Catalysis Today, 151 (2010) 237–243)

2- Reaction of NO, NH_3, and 0_2, over V_2O_5 on a TiO_2/SiO_2 catalyst as a function of temperature

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. As the SCR reaction is highly exothermal,it may also be evaluated by differential scanning calorimetry. With the quartz tube reactor simulating a conventional plug-flow fixed bed reactor, it is possible to measure the heat of reaction and simultaneously analyze on-line the reactants and products by mean of a mass spectrometer (Figure 4).

Such a MS-DSC coupling is used to investigate the reaction of NO, NH_3, and 0_2, over V_2O_5 on a TiO_2/SiO_2 catalyst as a function of temperature. Figure 5 represents the variation of the heat of reaction according to the temperature of reaction. The triangles represent data calculated from the composition of the gas mixture leaving the catalyst as measured with the mass spectrometer.

(J.J.P. Biermann, P.P. Coelen, H. Den Daas, F.J.J.G. Janssen, Thermochimica Acta, 144 (1989) 239–337)

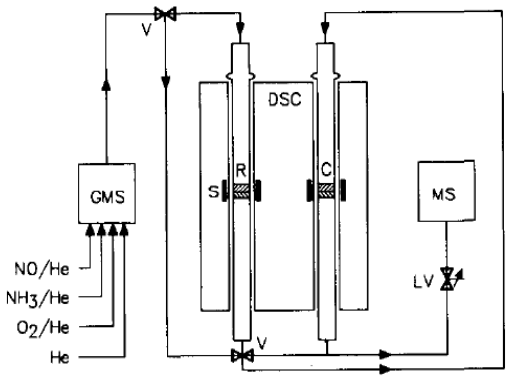

Figure 4 – TC, catalyst; GMS, gas-mixing system; DSC, differential scanning calorimeter; LV, leak valve; MS, mass spectrometer; R, reference; S, sensor; V, valve

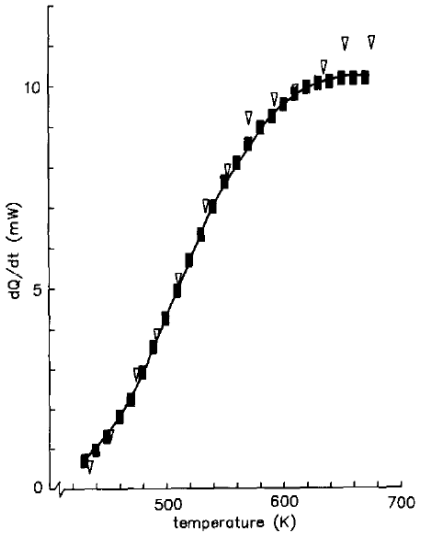

Figure 5 – Heat produced by the reaction of NO, NH_3, and 0_2, over V_2O_5 on a $TiO_{,2}/SiO_2$ catalyst as a function of temperature

3- Ammonia adsorption on a sulfonated polystyrene resin-type catalyst (Amberlyst 15)

The flow-through quartz tube is used to design a pulsed flow adsorption microcalorimeter (pulse-FMC) (Figure 6). Flow adsorption microcalorimetry (FMC) has advantages, such as its flexibility to allow changes in composition of the carrier gas and to vary the gas flow rate, and as a result it can be used to mimic industrial processes more realistically. Helium is used as the carrier gas and the 1% NH_3/He mixture is used as the probe gas. Pulses of probe gas are delivered to the carrier gas stream from a calibrated sample loop using a 6 position valve with microelectric actuator. The ammonia concentration in the gas stream is detected by a downstream thermal conductivity detector (TCD). It enables to measure the amount of ammonia (from the pulse) that is not irreversibly adsorbed on the catalyst. An exmapel is given with the ammonia adsorption on a sulfonated polystyrene resin-type catalyst (Amberlyst 15) (Figure 7)

(S.P. Felix, C. Savill-Jowitt, D. R. Brown, Thermochimica Acta, 433 (2005) 59–65)

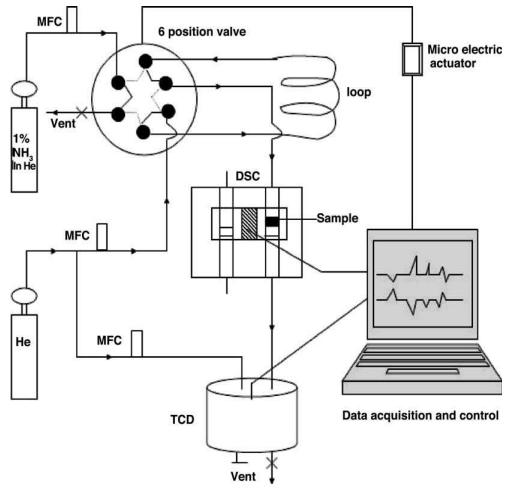

Figure 6 – Pulsed flow adsorption calorimeter system

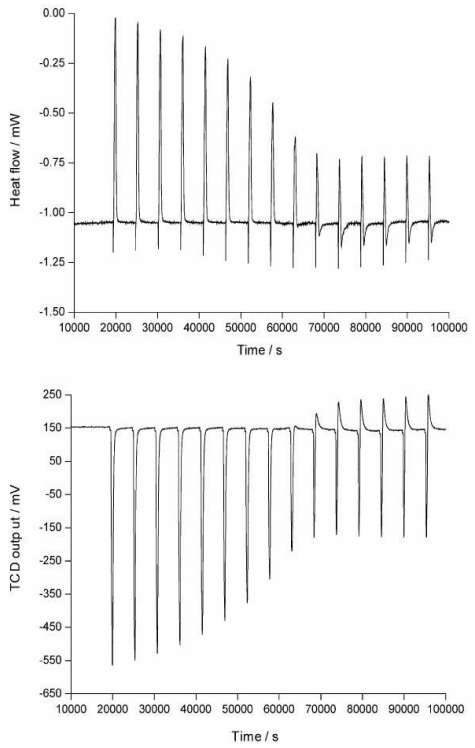

Figure 7 – Typical pulse-FMC data for the ammonia adsorption on Amberlyst 15 at 100 °C and 2ml min−1 flow rate and corresponding TCD data

4- Catalytic oxidation of propane

The conventional calorimeter Sensys DSC, used with the quartz tube reactors, is very well suitable for the investigation of catalytic bulk preparations in a wide temperature range (Figure 8). In particular, the illustration with the catalytic oxidation of propane demonstrates the interesting possibilities of the calorimetric investigations for the optimization of the catalytic features of biotemplated preparations. The investigated platinum nanoclusters were prepared based on biotemplating by bacterial surface layer proteins (S-layer) of *Bacillus sphaericus.*

Different catalysts are compared for the oxidation of propane (Figure 9)

$C_3H_8 + 5O_2 \rightarrow 4H_2O(g) + 3CO_2$

The catalytic activity of the S-layer based Pt catalyst is comparable with a platinum catalyst on aluminium oxide (without S-layer) as a reference system. An industrial used platinum catalyst has a significant lower activity in the considered temperature range for the chosen oxidation reaction

(R. Hüttl, F. Ullrich, G. Wolf, A. Kirchner, M. Mertig, W.Pompe, Thermochimica Acta, 440 (2006) 13–18)

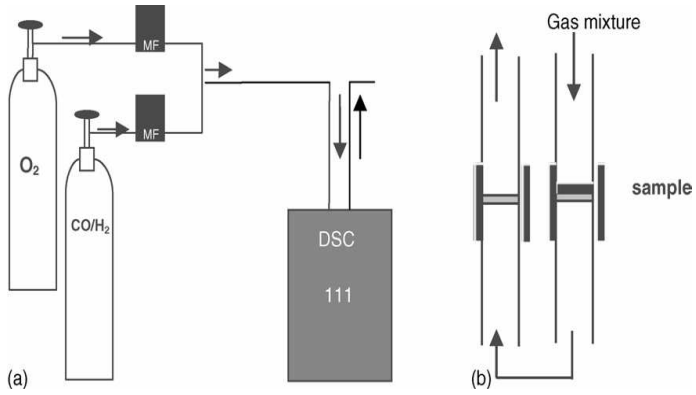

Figure 8 – (a) Mixing of the different gases, (b) Gas flow within the quartz tube reactor

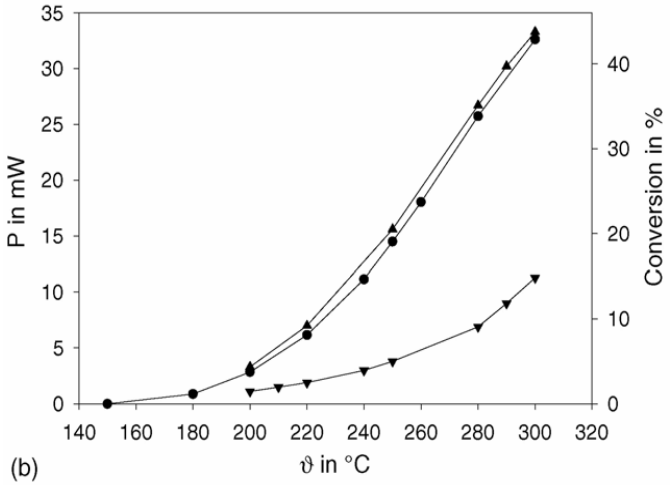

Figure 9 –Catalytic oxidation of propane (gas flow: 5 ml/min, C_3H_8 1 vol%, Pt in the bulk ~85g) with different catalysts
(●) Pt S-layer on aluminium oxide (A1); (▲)Pt on aluminium oxide, without S-layer (C); (▼)Commercial catalysts F221 from the firm Degussa, Pt on aluminium oxide

5- Interaction of carbon monoxide with zeolites

The zeolites are well known as substances that are extensively used as catalysts or adsorbents in many catalytic reactions. Fundamental approach of the understanding of their catalytic capacities involves the characterization of their active centers. The calorimetric measurement allows direct determination of the distribution of the strength of active centers.Carbon monoxide is often used as a probe for such determinations.

The experiment is done with the Sensys DSC using the quartz tube reactor on a Cu-zeolite (Figure 10). CO is introduced at 25°C on the zeolite via the pulse mode (injection loop of 0.2 ml).The calorimeter is connected to a mass spectrometer. If the MS does not detect any CO amu signal, it is a clear indication that the injected CO voulme is fully adsorbed on the zeolite. In the same way, when a CO amu signal is detected (and after calibrating the MS signal), the amount of CO that has effectively adsorbed on the zeolite is calculated. From these DSC and MS data, it is possible to draw the variation of the heat of adsorption of CO on the zeolite according to the surface coverage (Figure 11)

(V.M. Rakic, V.T. Dondur, R.V. Hercigonja, Thermochimica Acta, 379 (2001) 77–84)

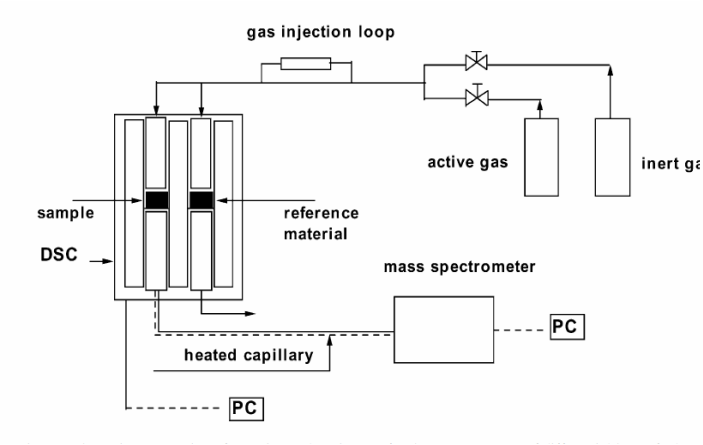

Figure 10 – Schematic representation of the Calvet type DSC with the injection loop and the MS coupling

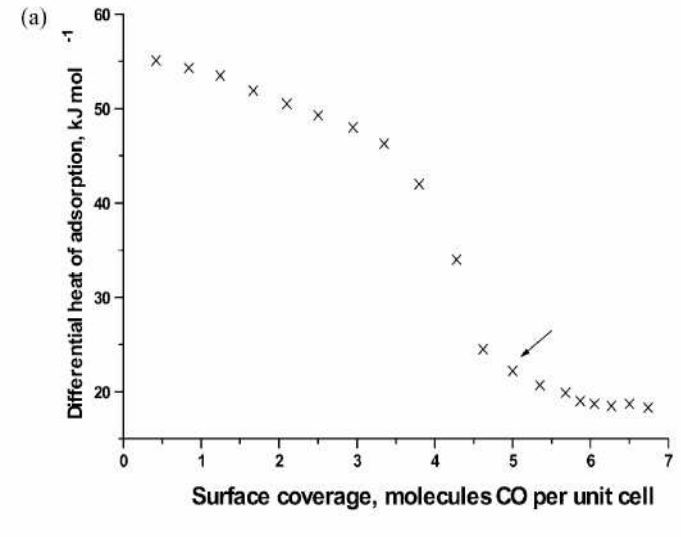

Figure 11 – Differential heats of adsorption of CO on CuY as a function of surface coverage

Conclusion

The adaptation of a flow reactor on the Calvet type DSC enables to open a large range of applications for the investigation of catalysts and adsorbents with various types of gas in the dry state but also in the humid state. It gives also the possibility to follow a heterogeneous catalytic reaction with on-line analysis of the products that are obtained from the reaction.

For investigations of adsorption/desorption in the static mode, Setaram has developed a silica glass finger, adapted to the Sensys DSC to work under normal pressure or vacuum. This vessel is also designed for the coupling between the Sensys DSC and a volumetric equipment in order to get a simultaneous measurement of the adsorbed volume and the corresponding heat of adsorption. A metallic pressure version (200 bar) is also available for investigations up to 800°C.

Figure 12 – Silica glass finger and the adaptation to the Sensys DSC

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