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Novel high-temperature, high-vacuum, all-metal sample cells for microcalorimetric measurements of solids

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The design of a novel microcalorimetric sample cell which allows rapid transfer of heat from the sample to the cell wall is described. The solid sample is dispersed around the internal walls of the cell. Since the thermopiles of the microcalorimeter are in contact with the outer surface of the cell, the new design of the cell allows rapid recording of the heat generated by the sample. The robust all-metal cell allows *in situ* sample activation under conditions of high vacuum and at temperatures up to 500 °C. The dispersion of the sample avoids any ''deep bed'' effects where gas may not be able to diffuse freely to the surface of all of the sample, which may be the case when a thick layer or plug of the sample is used. The cell enables faster acquisition of heat data and minimizes effects of self-heating of the sample. A simple tool, which assists the introduction of the solid sample into the cell and a compact resistor-element, which fits inside the cell for calibration, are described. [S0034-6748(97)04812-0]

I. INTRODUCTION

Microcalorimetry is a valuable tool for the determination of the acidic and basic properties of catalytic materials. Measurement of the heats associated with the adsorption (or desorption) of basic[1–4] and acidic[5,6] gases on to the catalyst gives a direct indication of its acidity or basicity, respectively. Calorimetry is the only *direct* method of measuring enthalpies, and is the source of reliable data, provided proper calibration has been performed and stable ambient conditions prevail. Ambient conditions are never really stable for long periods of time, thus the faster that heats of adsorption can be measured, the less error will be inherent due to changes in the ambient conditions (i.e., laboratory temperature). Microcalorimetric measurements are notoriously time-consuming and may require days for a single measurement.

Microcalorimetry finds numerous applications in various scientific disciplines besides the catalytic applications which were mentioned above. Physico-chemical quantities and processes such as specific heats, thermal diffusion coefficients, thermal conductivities, and heats of solution, dilution, mixing, and gelatinization may be analyzed using microcalorimetry.[7] Thermodynamic and kinetic parameters for chemical reactions may be determined through microcalorimetric measurements.[8] Biological applications are widespread, particularly studies of thermogenesis of plants, bacteria, and animals.[7,9] A relatively large amount of research has been carried out recently using microcalorimetry to test the stability of industrial products,[10] particularly pharmaceuticals,[11] explosives, propellants, and batteries.[12] The determination of sticking probabilities and heats of adsorption of gases onto metal single-crystal surfaces has recently been achieved using a novel design of microcalorimeter,[13] while heats of adsorption of gases onto supported metal particles have been measured using conventional microcalorimetry.[14]

For measurements which involve the adsorption of gases onto solid samples (e.g., catalysts), pretreatment of the sample under conditions of high vacuum and high temperature is usually required to remove traces of adsorbed species and water and to generate the ''active'' form of the catalyst. Commercially available calorimetric cells are generally not compatible with high-temperature sample treatment and/or operation under high vacuum, and do not allow for adequate dispersion of the sample around the walls of the vessel. Thus, samples may not be effectively or completely activated during pre-treatment which could lead to erroneous results. In addition, any heat which is evolved by the sample upon adsorption of a probe gas will not be conducted quickly to the thermopiles, resulting in a slow response. Self-heating of the sample, if dispersion is not adequate, may disturb the measurements by, e.g., inducing desorption of adsorbed species, which results in a thermal effect opposite in nature to that of adsorption (therefore the measured heats of adsorption would be lower in magnitude than the true value).

In this article, the design of a novel sample cell for use with commercially available microcalorimeters is described, which allows rapid thermal response and high-temperature and high-vacuum compatibility. A simple tool which assists in assembly of the cell and allows the sample to be easily introduced and a compact resistor-element which fits inside the cell for calibration are described.

II. CELL DESIGN

All components of the cell are constructed from high-grade stainless steel, and may be gold-plated to allow greater heat conductivity and resistance to corrosion by aggressive chemicals. The cell, together with the removable cell insert are shown in Fig. 1, where some of the key dimensions (in mm) are given. The outer body of the cell consists of three separate pieces; the main body (A), in which the cell insert and sample sit, the collar (B) which screws onto the main

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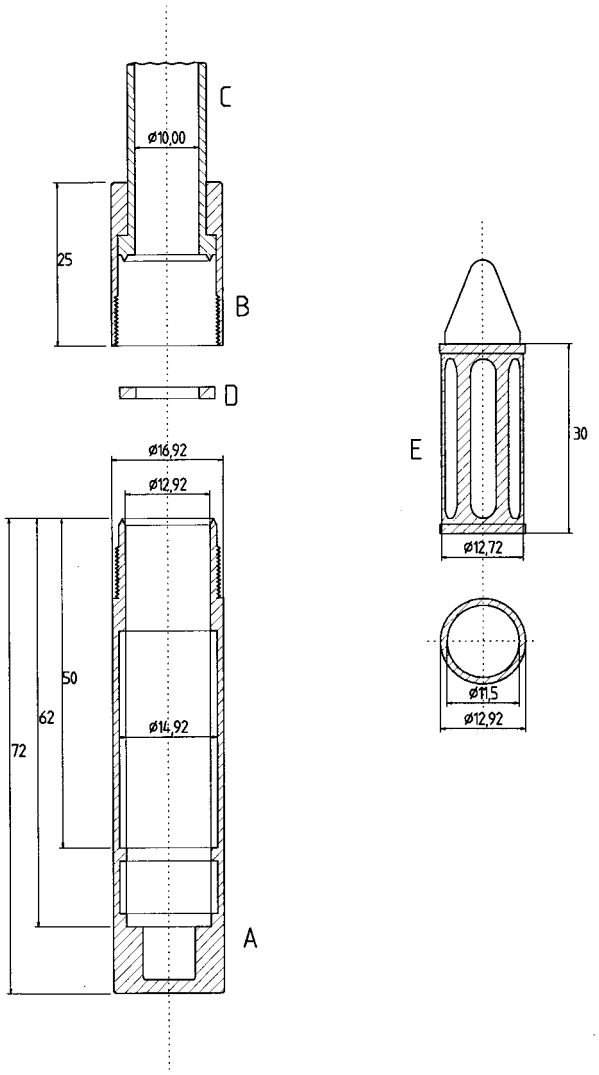

FIG. 1. Schematic representation of the calorimetric cell and cell-insert. (A) main body; (B) collar; (C) tube; (D) soft-copper gasket; (E) cell insert. Dimensions are in mm.

body, and the tube (C) which connects the cell to the vacuum and probe-gas preparation system. In addition, a replaceable soft-copper gasket (D), which forms a high-vacuum seal, is compressed between the two knife edges which are on the main body and on the tube.

The collar may rotate relative to the tube, so that the cell may be screwed together while not allowing the knife edges to rotate relative to one another. This is important for obtaining a good vacuum and avoids the necessity to over-tighten the cell, which could cause damage. Slots are cut into the bottom of the main body and top of the collar (not shown in the figure) to allow tightening of the cell with spanners. A special cell-supporting device may be used which holds the main body (A) and tube (C) rigid while the collar is turned using a spanner.

The tube is of large internal diameter to allow the attainment of a good vacuum in the cell during sample activation prior to microcalorimetric measurements. The thickness of the tube wall is kept to a minimum to reduce thermal conductivity between the cell and the laboratory. To allow

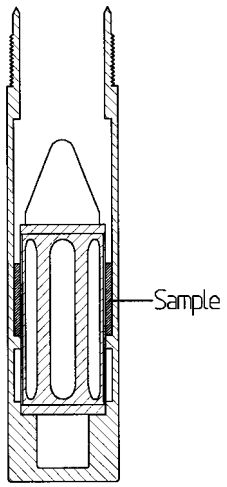

FIG. 2. Main body of the cell with the insert in position. The volume occupied by the sample is indicated.

sample pretreatment to be performed external to the microcalorimeter without exposing the sample to air, the top end of the tube may be fitted with a high vacuum valve. With high-temperature microcalorimeters, pretreatment in the calorimeter itself is possible, however, due to the generally slow heating and cooling rates, this is not desirable. If this type of cell is to be used in a high-temperature microcalorimeter at temperatures above 200 °C, the outer diameters of the main body and collar need to be reduced slightly to allow for expansion of the metal.

The cell insert (E) is a hollow, cylindrical, open-ended tube, the walls of which have had several slots cut into them to allow uninhibited diffusion of gas from the inside to the outside of the tube. Ideally, the surface area of the remaining tube-wall should be minimal. The short sections at the two ends of the tube are of slightly larger outer diameter than the rest of the tube (see Fig. 1). This is to allow stainless-steel gauze (50 μm mesh size, or similar) to be wrapped around the middle of the tube, and spot-welded into place. The resulting cylinder has a uniform outer diameter along its entire length. This design allows the solid sample to be confined between the outside of the insert and the inner wall of the main body, while the probe gas can diffuse freely through the insert. The stainless-steel gauze has been omitted from the figures for clarity. A stainless-steel loop is connected to the top of the insert to allow it to be removed easily from the main body of the cell.

The volume occupied by the sample is identified in Fig. 2, which shows the cell insert in position within the main body. The sample sits as a thin, loosely packed film ($\sim$1 mm) in contact with the internal wall of the cell. Because of the restriction in the main body approximately 50 mm from the knife edge (see Fig. 1), the sample is constrained to a height near that of the middle of the cell and hence near the middle of the microcalorimeter's thermopile. The sample is kept distant from any areas of the cell which possess large heat capacities (e.g., large masses of metal). Thus the majority of the heat generated at the sample is conducted directly through the cell walls to the thermopiles and does not con-

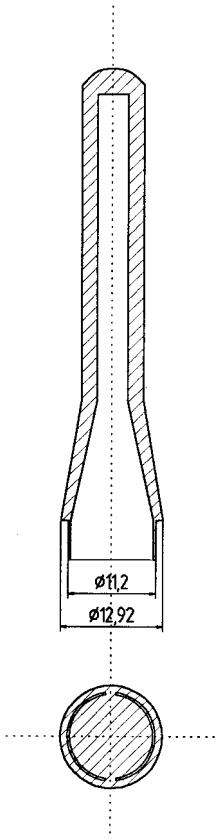

FIG. 3. Sample-introducing tool.

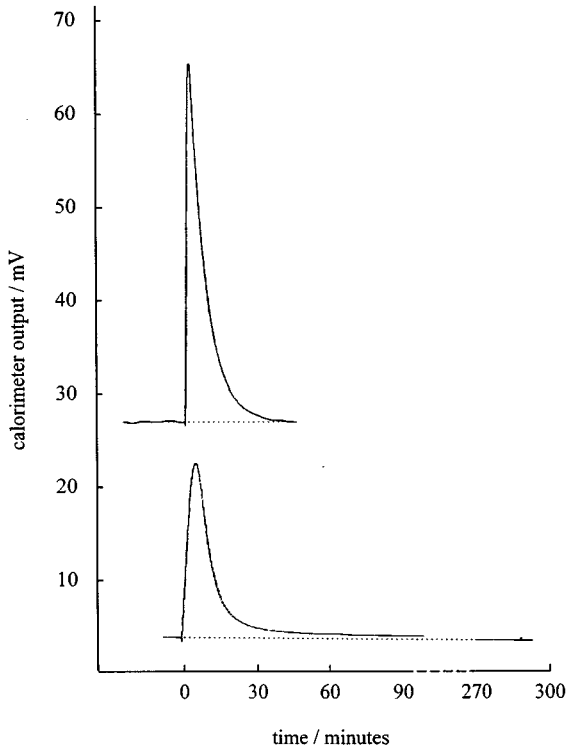

FIG. 4. Comparison between the thermokinetic curves of the new cell (upper curve, FWHM: 6 min, peak height: 38 mV) and another cell where the sample is not dispersed around the cell walls (lower curve, FWHM: 9 min, peak height: 18 mV). The curves have an arbitrary vertical offset.

tribute to heating of the cell itself. The thickness of the walls of the main body is kept to a minimum to ensure rapid conduction of heat from the sample to the thermopiles, while reducing the amount of heat which flows through the metal to other parts of the cell.

The dimensions indicated in Fig. 1 relate to the use of the cells in an isothermal differential microcalorimeter, type MS-70 (which can be regulated at temperatures between ambient and 200 °C), supplied by Setaram, Lyon, France. The overall height of the cell (main body + collar + copper gasket) when assembled is ~85 mm. The thermopile of the calorimeter is 80 mm in height and extends from the bottom of the sample cell to near the top of the collar when the cell is in place within the calorimeter.

The sample introducing tool is shown in Fig. 3. When in use, the tool sits on top of the cell insert when the latter is in place within the main body, such that the thin-walled section at the bottom of the tool sits inside the insert. Two slots, at 180° to one another, in the thin-walled section of the tool allow the loop of the insert to protrude into the tool. When the sample is then introduced, it is directed around the outside of the insert, where it is in contact with the cell wall. The tool may also be used to help seat the insert properly in the main body of the cell prior to introduction of the sample.

III. PREPARATION AND INTRODUCTION OF THE SAMPLE

The sample, either in the form of a powder or pressed lightly and cut in to tiny platelets (depending upon the particle size of the sample and mesh-size of the gauze chosen for the construction of the insert), is introduced when the insert is in place in the main body of the cell and the introducing tool is connected to the insert. The sample is simply introduced through the top of the main body, and the cell is tapped gently to allow the sample to fall into place. Once the sample is in place, the introducing tool is removed and the weight of the sample may be determined. The main body and insert, with the approximate dimensions given in Fig. 1 and constructed from stainless steel, have a combined weight of approximately 60 g, so that an analytical balance may be used. The amount of sample which is introduced will depend upon the type of measurements to be made and the nature of the sample; for measurement of the acidic properties of zeolites by adsorption of ammonia, samples of 50–100 mg are normally used.

The main body is then screwed on to the collar, with a copper gasket between the two. A small amount of high-temperature grease (e.g., MoS_2) is used to lubricate the screw thread and the areas where the collar rotates against the tube during assembly. The sample may then be activated in the cell under conditions of high vacuum and high temperature, and microcalorimetric measurements performed.

IV. OPERATING CHARACTERISTICS OF THE CELL

Figure 4 compares the thermokinetic response curve (heat recorded versus time) for the new design of cell with that of another design, where the sample is not dispersed around the cell walls. The data are taken from actual experi-

ments where ammonia gas was adsorbed onto an activated zeolite catalyst (H-mordenite). The amount of ammonia dosed onto the sample was similar in both cases, and the degree of catalyst coverage was approximately the same before each dose. For such measurements, a calibrated dose of gas is admitted simultaneously to the sample and reference cells. The heat which is generated through interaction of the gas with the sample is registered by the thermopiles of the calorimeter, giving an output in mV. This potential is integrated over the duration of the measurement, i.e., until the potential returns to the baseline value. The evolved heat corresponding to this integrated potential is known through a heat calibration, as described in the following section. The amount of gas admitted and the total heat generated being known, it is easy to calculate the enthalpy of interaction between the solid and the probe-gas. Once one measurement is complete, the next may be initiated by introduction of a further calibrated dose of gas. The acidic (or basic) sites of the zeolite are thus titrated, and a plot of acidic (basic) site strength *versus* adsorbate loading may be generated.

As is evident from Fig. 4, the full width at half-maximum (FWHM) of the thermokinetic peak is smaller (upper curve) for the new cell (i.e., 6 min vs 9 min), and the baseline has been re-attained in less than 1 h, as opposed to nearly 5 h for the other cell design (lower curve). The thermokinetic peak for the new cell is more symmetrical than that from the old cell, returning promptly to the baseline. The peak measured with the old cell possesses a very long tail, during which the potential of the thermopiles slowly approach the baseline. This is ascribed to poor design of the cell, where diffusion of the heat generated away from the sample is limited, and large masses of metal absorb most of the heat. Note that the time axis has been interrupted in the figure. The respective peak heights for the new and old cells are approximately 38 and 18 mV. In practice, the new cell has enabled microcalorimetric measurements of the adsorption of basic gases onto zeolite catalysts as a function of coverage to be completed in 4 days, as compared to 8 to 16 days when using the other cells. More details of how typical experiments are performed may be found in Ref. 15.

V. DETERMINATION OF THE HEAT-CONSTANT FOR THE CELL

In order to calibrate the cell for it's heat constant, a resistor-element was developed which could be placed in the cell, with the insert in place. Once in position, a known current at known potential is passed through the resistor-element for a known amount of time using a constant-current power source. The heat recorded by the microcalorimeter's thermopiles could then be related to that actually supplied by the resistor-element. This procedure was carried out in the absence of a sample. The resistor-element is comprised of three resistors connected in parallel (forming a unit of resistance approximately 1000 Ω) which were attached along the outside of a short length of flexible Teflon tubing, of a diameter small enough to just fit inside the cell insert. Thus, when in position, the resistors were gently pressed against the stainless-steel gauze, on the inside of the cell insert. Ideally, the resistors should be placed exactly where the sample resides, i.e., outside the insert, in contact with the cell wall, but this was not possible due to restricted access. Since the cells are always used in pairs (one contains the sample and the other is an empty reference cell), two such resistor elements were fabricated such that the cells would be balanced, although power was only supplied to the element in the sample cell.

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