

Adsorption micro calorimeter

Design and electric calibration

V. García-Cuello · J. C. Moreno-Pirajan ·
L. Giraldo-Gutiérrez · K. Sapag · G. Zgrablich

ICTAC2008 Conference
© Akadémiai Kiadó, Budapest, Hungary 2009

Abstract In this work, it is described an innovative heat flux micro calorimeter Tian-Calvet type designed to measure adsorption heats and reactions as well as adsorption isotherms. It consists in an adsorption instrument for volumetric gases, which is coupled to the micro calorimeter. The changes in the pressure are monitored by means of high sensitivity and high precision pressure transducers. The micro calorimeter has thermo elements that work by a Seebeck effect, in a twin cells system. The cells are inside a box in which the temperature can be adjusted from 77 to 300 K. The sensitiveness of the calorimeter is established by applying a perfectly known electric work. The results corresponding to the electric calibration, the base line stability determination and the time constant in the equipment are shown.

Keywords Adsorption calorimetry ·
Pressures transducers · Calorimeter constant ·
Time constant

V. García-Cuello · J. C. Moreno-Pirajan (✉)
Grupo de Investigación en Sólidos Porosos y Calorimetría,
Departamento de Química, Facultad de Ciencias, Universidad de
Los Andes, Bogotá, Colombia
e-mail: jumoreno@uniandes.edu.co

L. Giraldo-Gutiérrez
Departamento de Química, Facultad de Ciencias, Universidad
Nacional de Colombia, Bogotá, Colombia

K. Sapag · G. Zgrablich
Instituto de Física aplicada (INFAP), CONICET, Universidad
Nacional de San Luis, San Luis, Argentina

Introduction

The measurements of the adsorption heats over porous solids give chemical information about the strength in the chemical bonds involved in a variety of adsorption and catalytic processes. From a careful selection of the probe molecule it can be compared the strength between the structural chemical bond and the adsorbate and the behavior of some materials, like adsorbents and catalysts. In some cases, like ammonia and pyridine bases, this information leads to a better knowledge and the quantification of the acidic-base properties for metallic oxides [1–4] and the CO adsorption on metallic surfaces that can be used to probe the strength in the metal-carbon bond in hydrocarbons reactions over metallic catalysts [5].

The calorimeters that measure the total heat can be used to study the surfaces properties of solids. However, in some cases, the solids can exhibit heterogeneity in their surface and a fraction in the surface sites can determine the behavior of this solid in adsorption or catalytic processes. In consequence, it is desirable the determination of the adsorption differential heat in function of the surface cover. This kind of measurements can be determined with a flux micro calorimeter Tian-Calvet type [4, 6–8]. This work describes the design, construction and operation of an adsorption micro calorimeter that can be used to study catalyst, and the manner in which the electric calibration was made.

Methodology

Equipment general description

This calorimeter is based on designs published by other researchers and in the experience of our laboratory [9–19]

in the construction of such equipments. It is outlined the versatility and low cost of these equipments. The micro calorimeter described in this work can be operated from 77 to 500 K, keeping a high stability level in the base line signal at different temperature ranges. This wide temperature operation range is desirable to probe weak adsorption sites at low temperatures and strong adsorption sites at high temperatures. In particular, low temperatures are required to achieve significant adsorbate covers in weak adsorption sites at typical dosage pressures, for example $<10^3$ Pa, and to probe energy sites, where the surface is unstable or the probe molecules suffer decomposition at high temperatures. Higher temperatures are necessary to achieve enough surface mobility to permit the adsorbate molecules get equilibrium with strong adsorption sites.

The heat generated during the adsorption from a certain quantity of dosage gas causes a small difference in the temperature that is measured by thermal unions in a Seebeck effect, and produces a voltage signal that is proportional to the heat flux. This voltage, in the region of micro volts is captured with a type GPIB card that amplifies the signal and storage the data in a PC. Two calorimetric cells are employed. The sample cell contains the system under study and the reference sample is a blank used to minimize the heat flux signals caused by the gas dosage inside the system and the temperature fluctuations in the heat deposit.

In Fig. 1a and b, it is shown a schematic diagram of the cells and the peripheral equipment and detail of the contact between cell-sensors. The system is set to achieve a vacuum of about 10^{-4} Pa. A portion of the dosage section is constructed in Pyrex glass using valves with a hermetic seal to avoid leaks. To minimize the gas leaks and have a better control on their dosage, the glass system is coupled to a stainless steel device with high precision valves. It is necessary to put a valve between the dosage section and the calorimetric cells, to control the gas injection velocity. The leak velocity is kept under 10^{-1} Pa min^{-1} to ensure exact measurements of the equilibrium pressures and to minimize the contamination of the sample with atmospheric oxygen. The connections between the glass and the steel devices are specially made with O-rings to avoid gas leaks. When the electrical calibration is realized, the cell is replaced by the electrical resistance.

The calorimeter is compound by a metallic central block that acts as a heat deposit constructed in aluminum and isolated from the surrounding, to keep the temperature of interest, and two thermal transducers imbedded in an aluminum block assembled in a twin-type system, in order to operate as the sample and the reference cells. The sensors are put into the aluminum block and are perfectly adjusted to annual air convection currents that could generate fluctuations in the base line, which is a contribution from this design compared to other calorimeters reported in the

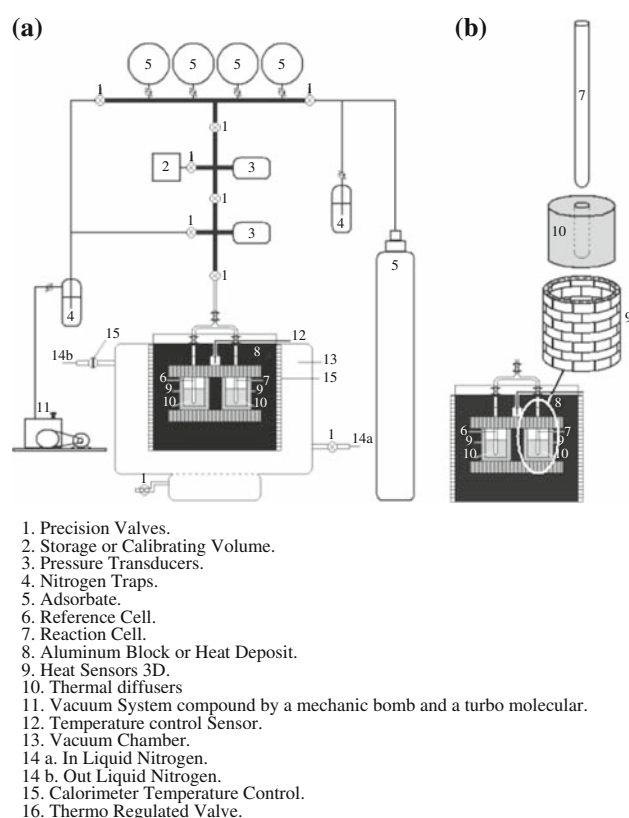


Fig. 1 **a** Schematic diagram of the calorimetric system. **b** Details of the contact between cell-sensors

bibliography [1]. The high thermal conductivity and the big mass of the aluminum block adds enough stability to the equipment in the base line to integrate the signals of the heat response curves generated by the dosage of some micromols of gases. The aluminum block is surrounded by a heater constructed with mica, which is connected to a power source and isolated from the stainless steel chamber that is useful to work at temperatures about 77 K. A temperature controller keeps the block in the desired adsorption temperature range ± 0.1 K.

The heat flux signals are measured by assembling the transducer, which is built under required specifications by the International Thermal Instruments Corp.TM (Del Mar, CA). Each unit contains thermo batteries that consists on hundreds of thermo elements that operate under the Seebeck Effect, connected in series in a “thimble-type” configuration that permit completely surround the glass-built calorimetric cells (these cells are interchangeable by similar ones built in stainless steel) and providing their remove for treatments at high temperatures. A thermal diffuser plate, inserted between the cell and the thermo battery, provides a good heat distribution through the thermo battery surface. The thermal transducer units both in the sample and in the reference should have units with similar

sensitiveness. To correctly evaluate the thermal effects signals, it is necessary to properly study the base line stability of the thermo elements signals.

The samples are put into the calorimetric cells by a 5 mm diameter glass tube (or stainless steel). The maximum accepted value is 5 cm³, which corresponds to 2 mm of the 30 mm long cell, as 20 mm do not have contact with the thermo elements. The samples, especially powders, can be compressed (10^7 – 10^8 Pa) to improve the layer conduction or the inter-particle diffusion of the adsorbate molecules.

Design of the calorimetric cell

Taking into account that the quartz is a poor heat conductor compared to metals, it is useful to built glass cells as thin as possible in those walls in contact with the heat flux sensors. The design of this equipment is simple. It consists in a 5 mm diameter and 40 mm long cells with walls made of glass and stainless steel, which are coupled easily and hermetically to the built adsorption system. These cells are used for treatments of samples with static gases.

Heat signal calibration

The calibration of the heat flux transducer that surrounds the sample cell is necessary to convert the voltage-time response signal in energy units. The two following experimental designs were employed to calibrate the calorimeter: (a) electrical calibration and (b) chemical calibration.

An AgilentTM voltage source E3649A model supplies the potential through a 640 K Ω resistor built to adjust perfectly with the heat flux sensors, to simulate the thermal effects generated in each gas addition to the adsorbate under study. By means of a 6½ figure Agilent 34401 multimeter is recorded the voltage level and determined the power that feed the calorimeter. The sensitiveness of the calorimetric equipment is calculated from its constant, which is determined by applying pulses at different voltage levels or by stationary state. The calorimeter chemical calibration is made by CO₂ adsorption in a ZSM5 zeolite characterized previously by volumetric adsorption techniques.

Results and discussion

The heat flux sensors sensitiveness is determined setting the calorimeter constant by the application of pulses at different voltages and by stationary state generating typical calorimetric response as shown in Figs. 2 and 3 respectively. In Fig. 2 calorimetric response it has been magnified the base line signal part to illustrate its stability with a value of ± 0.5 μ V for a voltage of 0.42 v. This, demonstrate the heat flux sensors signal stability under this work conditions.

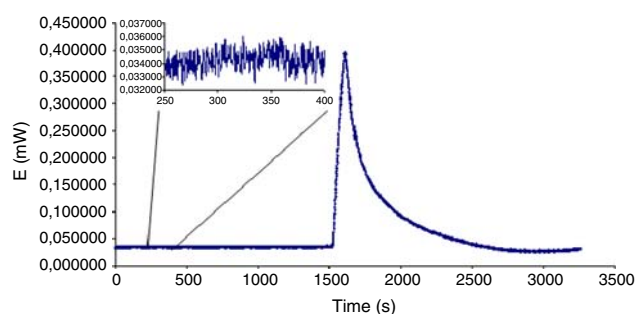


Fig. 2 Calorimetric response obtained by the potential pulse method in the calorimeter

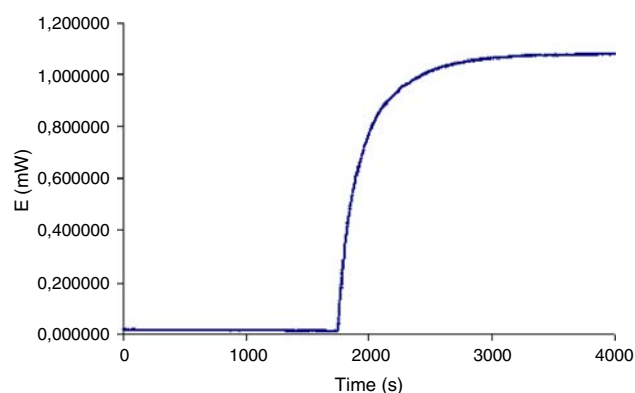


Fig. 3 Calorimetric response obtained by the application of a potential constant pulse for the built micro-calorimeter

It is important to determine in a calorimeter the characteristics of the sensors of flow heat due to the that they allow to establish the sensibility and precision of the equipment. In agreement to these parameters there can be deduced that type of studies can realize with the equipment; sensors that allow to have a level of low noise in the line base as the case of the present investigation and with small constants of calibration, which indicate a good sensibility, it will be allowed that the calorimeter should be used in studies where the thermal effects of the chemical or physical interactions are small, and due to the mentioned characteristics they will do that the calorimeter could register the thermal effects of these interactions.

It is necessary mention that to realize the determination of the constant of electrical calibration, the position of the resistance used to realize the dissipation of the electrical work to the interior of the cell calorimetric is important in this equipment; in conventional calorimetry the resistance must be placed in an equidistant way with regard to the position of the heat sensors. Nevertheless in this work this situation does not appear, due to the fact that the calibration resistance was designed of such a fetters that fits physically to the size of the cell of reaction, for what the position remains fixed always.

Table 1 Calibration constants obtained for the microcalorimeter by the potential pulse method

Applied Electrical Work/J	Electrical Power/mW	Calibration constant, K/mW V ⁻¹ *
1.500	1.500	7700.0 ± 0.3
1.000	1.000	7900.0 ± 0.2
0.750	0.900	8000.0 ± 0.1
0.500	0.700	8200.0 ± 0.1
0.250	0.125	8400.0 ± 0.2
0.125	0.020	8400.0 ± 0.2

* Each reported value corresponds to a media of 20 measures and a confidence limit of 95%

Table 2 Calibration constants by stationary state obtained for the microcalorimeter

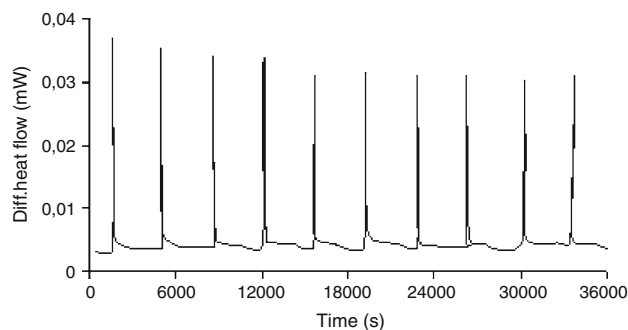
Applied voltage/V	Electrical power/mW	Calibration constant, K/mW V ⁻¹ *
0.125	0.025	7200.0 ± 0.1
0.200	0.065	7400.0 ± 0.3
0.350	0.325	7700.0 ± 0.5
0.700	1.300	7800.0 ± 0.3
1.000	2.995	7600.0 ± 0.3
1.250	5.000	7400.0 ± 0.4
1.699	8.255	7400.0 ± 0.2

* Each reported value corresponds to a media of 20 measures and a confidence limit of 95%

In Tables 1 and 2 are shown the results obtained for the calibration of the heat flow sensors, applying different potential levels and a fix potential to evaluate the equipment constant, at times between 100 and 16 s. It is observed that the micro calorimeter constant value keeps constant in the applied potential flow range.

Similar results were obtained when the equipment was operated with gas injections (CO₂ in this case). From this, it is deduced that the sensitiveness (1/K) is 125 μV mW⁻¹ (with a confidence limit of 95%). It is necessary to highlight that the sensitiveness of this equipment is higher than those reported by other authors with similar equipment [1–3].

In the Table 1 shows a variation between the values of the constants of calibration, this is owed the different levels of power that were dissipated across the electrical resistance to small values of electrical removed powers values are obtained of constants lightly major compared with regard to when there dissipated electrical major powers where there are achieved electrical small constants, which this one in good agreement with regard to results obtained in literature which shows that light major sensibility is reached when major powers dissipate

**Fig. 4** Adsorption microcalorimeter response for each CO₂ injection over the titanium oxide

Finally, to complement the equipment calibration and establish its response time it was realized and additional essay with commercial P25 (AEROXIDE®) titanium oxide, without compression. The results are shown in Fig. 4. Following the Tian Equation for a system with calorific capacity [4, 8], it is a first order type response time. It was evaluated the time constant (τ), to find the response to the changes when a power is applied, and it was 120 s in vacuum and 100 s at atmospheric pressure. The last condition corresponds to final pressure points in an adsorption experiment. It is important to emphasize that the integrated areas in the answer curves was identical, indicating that the calibrating constant energy was the same in both conditions and that the heat loss from the natural convection in the cells was not significant for the studied pressure ranges.

Conclusions

It was built an adsorption micro calorimeter at an affordable price, which is useful to measure adsorption heats and solid surfaces reactions. The equipment works in a temperature range from 77 K to 500 K. It was demonstrated experimentally in this work that it works at 298 K. Calorimetric cells in glass and stainless steel were prepared for the treatment of samples in static form. These cells enable the study of various catalysts in general. The time constants in vacuum and at atmospheric pressure were determined. These constants show that this equipment is useful to study processes with slow kinetic. The sensitiveness of the equipment is high. Finally the noise in the signal is very small and do not affect the measures.

Acknowledgements The authors are grateful to the agreement between Universidad de los Andes (Colombia) with Universidad Nacional de Colombia and Universidad Nacional de San Luis (Argentina), under which was carried out this work. Additionally Prof. Moreno wants to specially thanks to Universidad de los Andes for the assignation of a STAI, which was partially used to do this research.

References

1. Handy BE, Sharma SB, Spiewak BE, Dumesic JA. A Tian-Calvet heat-flux microcalorimeter for measurement of differential heats of adsorption. *Meas Sci Technol*. 1993;4:1350–62.
2. Aeroux A, Gravelle PC, Védrine JC, Rekas M. Microcalorimetry study of the acidity of H-ZSM-5 zeolite. In: Rees LV, editor. *Proceedings of the fifth international conference on zeolites*. London: Heyden; 1980, pp. 433–9.
3. Védrine JC, Aeroux A, Coudurier G, Englehard P, Gallez JP, Szabó G. Shape selectivity and acidity of ZSM-5 and ZSM-11 type zeolites. In: Olson D, Bisio A, editors. *Proceedings of the sixth international conference on zeolites*. Guildford: Butterworth; 1984, p. 497–507.
4. Cardona-Martínez N, Dumesic JA. Applications of adsorption-microcalorimetry to the study of heterogeneous catalysis. *Adv Catal*. 1992;38:149–244.
5. Gravelle PC. Calorimetry in adsorption and heterogeneous catalysis studies. *Catal Rev Sci Eng*. 1977;16:37–110.
6. O'Neil M, Louvrien R, Phillips J. New microcalorimeter for the measurement of differential heats of adsorption of gases on high surface area solids. *Rev Sci Instrum*. 1985;56:2312–22.
7. Parrillo DJ, Gorte RJ. Characterization of stoichiometric adsorption complexes in H-ZSM-5 using microcalorimetry. *Catal Lett*. 1992;16:17–25.
8. Calvet E, Prat H. *Recent progress in microcalorimetry*. Pergamon Press: Oxford; 1963, p. 1–167.
9. Iglesia E, Baumgartner JE. A mechanistic proposal for alkane dehydrogenation rates on Pt/L-zeolite, Inhibited deactivation of Pt sites within zeolite channels. In: *Proceedings of the tenth international congress on catalysis*, vol. 1. Budapest: Hungarian Academy of Sciences; 1992, p. 157.
10. Giraldo L, Moreno JC, Huertas JI. A heat conduction microcalorimeter to determination of the immersion heats of activated carbons into aqueous solutions. *Instrum Sci Technol*. 2002;30:177–86.
11. Giraldo L, Moreno JC. Design, calibration, and test of a new dissolution isoperibol microcalorimeter. *Instrum Sci Technol*. 2007;35:453–63.
12. Giraldo L, Moreno JC. Influence of thermal insulation of the surroundings on the response of the output electric signal in a heat conduction calorimetric unit. *Instrum Sci Technol*. 2005;33:415–25.
13. Huertemendía M, Giraldo L, Parra D, Moreno JC. Adsorption microcalorimeter and its software: design for the establishment of parameters corresponding to different models of adsorption isotherms. *Instrum Sci Technol*. 2005;33:645–59.
14. Garcia-Cuello V, Moreno-Piraján JC, Giraldo-Gutiérrez L, Sapag K, Zgrablich G. Design, calibration, and testing of a new Tian-Calvet heat-flow microcalorimeter for measurement of differential heats of adsorption. *Instrum Sci Technol*. 2008;36:455–75.
15. Vargas EF, Moreno JC, Forero J, Parra DF. A versatile and high-precision solution-reaction isoperibol calorimeter. *J Therm Anal Calorim*. 2008;91:659–62.
16. Giraldo L, Moreno JC. Calorimetric determination of activated carbons in aqueous solutions. *J Therm Anal Calorim*. 2007;89:589–94.
17. Ladino-Ospina L, Giraldo L, Moreno JC. Calorimetric study of the immersion heats of Lead (II) and Chromium (VI) from aqueous solutions of Colombian coffee husk. *J Therm Anal Calorim*. 2005;81:435–40.
18. Betancourt M, Giraldo L, Moreno S, Molina R, Moreno JC. Relation between immersion enthalpy and the acidity of clay pillared minerals. *J Therm Anal Calorim*. 2008;92:899–904.
19. Rodríguez GA, Giraldo L, Moreno JC. Calorimetric study of the immersion enthalpies of activated carbon cloths in different solvents and aqueous solutions. *J Therm Anal Calorim*. 2009;96:547–52.