Introduction

Gas–solid reactions relate one of the most important research subjects in sensors-actuators systems. Several specific sensors are described in the recent literature [1]. In fact, arrays of different sensors are in the basis of the chemical (or electronic) nose [2]. Mainly conductometric sensors (metal oxide, ionic conductor or conductive polymer) and quartz microbalances are used. Also it has been shown that integrated circuit microcalorimeters coated with a gas sensitive film can be applied for gas detection [3, 4]. The calorimetric improvements are related to ‘reactions’ between extremely lower masses [5, 6]. For instance, in analytical studies the actual target is situated close to several μg for mass of the reactants. Development of the calorimetric devices and the need of improved results for these lower masses induces two levels of difficulties: The first one is the use of highly sensitive elements as the Al–Si [7] thermocouples and appropriate auxiliary elements (i.e., pumps and temperature control) and the second one relates an improved outline of the devices and of the heat transfer formalism. In fact, the main target of this and previous papers I, II, III and IV [8–11] is the analysis of ‘calorimetric’ devices for improved quantitative results. By other hand, geometrical problems can also decrease the reability of calorimetric results [12].

The last, but not the least, relates the particular characteristics of the studied phenomena: liquid–liquid mixture, the gas–solid reaction, and so on. The former mainly requires the analysis of the steady state situation but the later is usually associated to transitory situations with increased difficulties in the formalisms.

Some qualitative and introductory observations are outlined. By one hand, two standard manufactured nano-calorimetric devices using two Xensor type chips. Finally we carry out a deeper analysis of the x–y effects on the calorimetric detector for dissipations in the reactant shell extremely close to the detector surface to visualize the link between the power density distribution and the output signal.

Keywords: accuracy, chemical nose, conduction calorimeters, gas–solid detectors, position effects

Gas–solid reactions in the field of solid-state gas sensors

Gas–solid reactions are the basis of many solid-state gas sensors which are mainly of resistive type. Solid-state resistive gas sensors may be based on bulk conduction or surface layer conduction. In the first case, gas–solid reactions modify the bulk stoichiometry which results in a bulk conductivity change. This principle has been applied to oxygen sensors for automotive exhaust. With the surface layer conduction, surface reaction with the gases modifies the concentration of the mobile electrical charges, which change the conductivity. The bulk conduction sensors are limited to the oxygen measurement and the response time is often slower, due to the stoichiometry
change which is related to a diffusion mechanism [13]. So, thin or thick films sensors based on a change of the surface conduction are preferred to the bulk ones. Moreover they allow better on-chip integration and mass-production, and are often cheapest.

Copper(I) bromide ammonia sensor is an example of how a specific gas–solid reaction can be used to implement a highly selective gas sensor. Copper(I) bromide CuBr is used for ammonia gas sensing, based on the reported existence of very stable Cu⁺–ammonia complexes in aqueous solution, such as \([\text{Cu(NH}_3\text{)}_2]^+\). This mixed conductor shows large Cu⁺ ion mobility and a modest electron hole conductivity of CuBr at ambient temperature. CuBr films can be prepared by magnetron sputtering [14, 15], but most efficiently by chemical reaction between Cu metal and an aqueous CuBr₂ solution [16]. Prior to use as sensor, the films must be conditioned few hours under an ammonia partial pressure of 100 mbar. This initial treatment is necessary to stabilize the films and get reproducible and long-time stable measurements. After the first exposure to a high ammonia concentration, the sensors are kept at ambient atmosphere. The sensor effect can be interpreted by a two-step mechanism:

1. A monolayer of chemisorbed NH₃ molecules is formed at the CuBr surface with Cu⁺ ions attracted to the surface during the initial ammonia treatment. The copper ion vacancy concentration is enhanced in negatively charged space charge regions that counterbalance the positive surface charge. These regions very easily percolate through the samples. They represent high conductivity regions, short-circuiting the bulk and strongly enhancing the film conductivity after the initial ammonia treatment.

2. After formation of a chemisorbed ammonia monolayer, further ammonia molecules are physisorbed during the sensor measurements. Physisorption relies on weak Van der Waals forces: the observed small decrease of the bulk conductivity may be attributed to dipolar effects (reduction of electron hole mobility). This step is totally recoverable and the initial conductivity is found after the ammonia gas stream is switched off.

A typical dependence of the electrical resistance of CuBr films on the ammonia partial pressure in the gas phase, at room temperature, is shown in Fig. 1.

A quantifying process between the resistance measurements and the energetic dissipation, requires tentative measurements determining an approach to working scales previous to some considerable effort need for building an improved calorimetric device inside the ‘open chamber’ used in surface analysis studies.

Calorimetric detection of gas solid reactions

In the case of energetic measurements the experimental system used was constructed using two Xensor LCM 2524 nano-calorimeter sensors [17]. The experimental device permits the simultaneous detection of the two signals produced by the same gas acting on two different polymers. The supply of the sample gas (synthetic air plus ‘guest’ gas) and of the reference gas (only synthetic air) is provided through tubes with labyrinth path inside a metallic element to ensure a homogeneous temperature. Each detector uses a half of the total gas flow. The experiment consists in measuring the absorption enthalpy in the solid–gas interaction when the sample gas reacts with the polymer, and the corresponding to degassing (or desorption enthalpy) when only the pure reference gas is used. From thermodynamic point of view two well definite states are necessary; i.e., completely degassed state (‘infinite’ time of degassing), and well defined time of reaction with known concentration.

For analyzing the heat loss by the flowing gas the following experiments were performed [18]:

- Measuring steady state Joule effects due to chip heater at constant heat power and different volume flow rate and different polymer thickness.
- Measuring the integral effects for the absorption and desorption of heptane for the given polymer at different flow rate, different polymer thickness and at fixed sample concentrations.
- Analyzing the nozzle direction effects by steady state Joule heating and absorption experiments at fixed flow rates and polymer layers but with different nozzle designs.

In the experiments series of transient heat power pulses are produced by periodical excitation of the