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REPORT ON THE WORKSHOP

"CALORIMETRY AND THERMAL ANALYSIS IN SURFACE SCIENCE AND CATALYSIS"

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Workshop leader: BICE FUBINI

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The subject of the workshop covered different techniques which can be divided into two main groups:

I) Adsorption calorimetry

This is usually performed under isothermal conditions and can be applied to both gas-solid and liquid-solid systems, obviously employing different equipment.
It covers investigations of physical adsorption, chemisorption and reactions in the bulk.
It is always necessary to relate the heat measured to the corresponding adsorbed amount in order to obtain molar values of the interaction energy.
For a complete characterization of the solid surfaces it is important to obtain the evolution of the heat with coverage which describes the building up of the adsorbed phase and which is representative of the distribution of active sites at the surface.

II) Temperature programmed techniques

These all consist in observing phenomena occurring by regularly raising the temperature of the sample.
They can be divided into two categories:

i. Methods capable of detecting modifications occurring in the adsorbed layer or at the surface. With temperature programmed desorption (TPD) the sample is saturated with the adsorbate at low temperature and, by raising the temperature, desorption occurs in such a way that each form of adsorption has a corresponding desorption peak. The number of adsorbed species and their activation energy are usually obtained in this way. Temperature programmed reduction (TPR) is employed with solid surfaces which may undergo reduction (e.g. oxides), by progressively heating the sample in flowing hydrogen. Information are obtained on the reducibility and on the presence of active oxidizing sites at the surface.

ii. Methods which give information on modifications occurring within the whole bulk upon increasing the temperature which are relevant to the surface properties of the final material obtained. The conventional thermal analysis techniques such as DTA, DSC, TG, are in fact largely used for the characterization of solids and in catalyst design in order to optimize the preparation route.

Thermal Analysis Highlights, 9th ICTA, Jerusalem, Israel, 21–25 August 1988.

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The first topic raised by the workshop leader was the possible future evolution of adsorption calorimetry and the reasons why this technique is so little used in surface science laboratories. The state of the art in fact reveals that, in spite of the fact that there is a definite need for energy data and site energy distribution, in research groups dealing with catalysts or with surface chemistry problems in general, very few laboratories are equipped for adsorption microcalorimetry techniques. This is particularly true for the United States for example where perhaps, because of readily available expensive and sophisticated techniques giving indirect energy values, adsorption microcalorimetry is employed in an extremely small number of cases.

The heat of adsorption in gas solid systems have already been measured for a long time. The instrumentation available, however, only allowed an overall measurement of the heat evolved when a surface was saturated with a given adsorptive. A remarkable improvement occurred in this field in the sixties when heat flow microcalorimeters of the Tian-Calvet type, very sensitive and stable over long periods of time, became available. In fact, before then, most heat of adsorption data were obtained merely by saturating the surface with the adsorptive, thus giving an overall heat of interaction. Only in very few cases the evolution of the heat of adsorption with coverage was evaluated. With heat-flow type calorimeters it became possible to follow precisely the evolution of heat with coverage, either by small successive increments in the adsorbate or by using a continuous feed of adsorptive, thus having access to site energy distribution, phase transition, etc.

As to the future, in addition to particular improvements in the instrumentation itself it seems reasonable to expect a greater employment of the technique and a systematic comparison of enthalpy values obtained calorimetrically with energy data originating from other sources.

There must be some good reasons, however, for the fact that the technique has been so little exploited.

Among the possible ones are the slowness of the experiment itself, the non-availability of commercial systems including an apparatus for measuring the adsorbed amounts and the necessity of coupling heat of adsorption data with information arising from other sources.

In fact it must be pointed out that, in contrast with new surface techniques which allow detection only of particular atoms or molecules (e.g. EPR, NMR, etc.) an overall heat measured during the adsorption process by means of a calorimeter can be comprehensive of any concomitant phenomenon occuring at the surface. The problem often is in fact how to isolate the required ΔH value from the heat measured, and how to relate the energy value obtained to a precise surface reaction.

These difficulties are particularly relevant when working on adsorption from solutions. Dr. Rouquerol (CNRS, Marseille, France) remarked that in such a case what is measured is always an enthalpy of displacement of the solvent molecules by the solute. It is indeed possible to measure rather precisely the amount of adsorbate (e.g. a surfactant) but the amount of solvent displaced (e.g. H_2O) remains generally unknown. The question is raised by Dr. Dollimore, University of Toledo OH, USA) whether by simulthaneous measurement of the heat of immersion in the solvent and the heat of adsorption from a solution the true ΔH of adsorption could be obtained. Dr. Rouquerol reported that a project in this direction is in fact going on in his laboratory in collaboration with Professor Everett (Bristol University, U.K.) and Dr. Wadso (Sweden): the system chosen is the adsorption of small molecules on graphon.

As to the combined use of thermal analysis technique (DTA, DSC, TPD, TG)with calorimetry Dr. Fubini remarked that a great deal could be achieved by combining these two kinds of thermal techniques, most data obtainable being complementary to one another.

In fact thermal analysis mainly furnishes kinetic data while adsorption calorimetry supplies equilibrium data, although equilibrium data can also be obtained by TPD in particular cases and kinetic information can be obtained from adsorption calorimetry. Dr. Dondur (Belgrad University, Yugoslavia) reported that in some cases a connection between heat of adsorption and activation energies for desorption, obtained with TPD, can be made.

Dr. Phillips (Penn State Univ, PA, U.S.A.) described the remarkable influence of the kinetics of adsorption on the values measured for the heat of adsorption when dealing with pseudo-equilibrium activated processes. He stated that with a mathematical model it is possible to predict the possibility of maxima in the heat of adsorption vs. coverage curves. Dr. Dollimore pointed out that in such a case a compensation effect should be invoked. Dr. Rouquerol reported that, as far as physical adsorption is concerned, maxima can be detected in correspondence to a phase transition of the adsorbed state. Dr. Fubini added that indeed very few cases of maxima have been detected with chemisorption, all corresponding to non-equilibrium states. A possible example is what was found on H-ZSM Zeolite upon adsorption of ammonia by Dr. Gravelle and coworkers (CNRS, Villeurbanne F.). In such a system, because of the narrow channels and of the high sticking probability of the probe molecule, the strongest sites located internally were saturated after the less strong external ones, thus presenting a maximum in the heat vs. coverage curve.

Dr. Fubini remarked that it would be very useful to have equipment which allows both the measurement of the heat of adsorption and a thermal programmed desorption to be performed on the same sample. Such a system would allow a complete investigation of the adsorbed species, its energy of interaction with the surface and the kinetics of adsorption and desorption. An enthalpy and activation energy value could thus be furnished for each form of adsorption.

There followed a series of contributions of the speakers on various topics.

— J. Rouquerol and Y. Grillet - Centre de Thermodynamique et de Microcalorimetrie, C.N.R.S. - Marseille - France.

Adsorption calorimetry from solution

Experiments may be carried out either in a batch microcalorimeter (specially suited for studies of the kinetics of adsorption and whatever the grain size of the adsorbent) or in a flow-through microcalorimeter (especially suited for studies of adsorption-desorption and allowing control at will of the final pH, ionic strength and composition of the solution in equilibrium with the adsorbent). Therefore, both approaches remain useful and are complementary to each other if one wishes, as usual in these experiments, to follow the build up and structurization (which may extend over hours) of the adsorbed layer. Most work, until now, seems to have been done on adsorption of surfactants and of smaller organic molecules from water solutions.

Adsorption calorimetry from the gas phase

This approach is more direct and more often oriented towards a direct characterization of the state of the adsorbing surface (although it also lends itself to very fine and sensitive detection of 2 D - phase changes in the adsorbed layer). This is done not only by chemisorption (of H_2O, NH_3, CO, O_2 ...) but also, in a most rewarding way, by simple comparison of Ar and N_2 adsorption, the latter giving rise to specific interactions with any polar site of the surface (hydroxyls, but also "uncovered" cations), due to its permanent quadrupole moment. A useful application is the determination of the proportion of polar faces in polycrystalline samples (kaolin, talc, ZnO ...).

— J. Phillips - Dept. of Chemical Engineering - Pennsylvania State University Pennsylvania - U.S.A.

Mathematical analysis of the effects of surface heterogeneity in chemisorption

An attempt to combine kinetic and heat of chemisorption data was presented. Two simple models of chemisorption were considered: kinetically controlled adsorption and equilibrium adsorption.

In the first mechanism it is assumed that adsorption occurs in parallel on several different types of surface sites, where the rate of adsorption at each type of site is controlled by site activation energy and concentration of the sites. It is in such cases assumed that true equilibrium between adspecies never occurs. In the second mechanism equilibrium among adsorbed species occurs rapidly. Using a set of differential equations solved numerically it was shown that if kinetics control the adsorption process the observed differential heats of adsorption will not necessarily decrease with coverage.

— D. Dollimore - University of Toledo - Ohio - U.S.A.

Surface studies with combination of thermal analysis techniques

Two aspects of calorimetry and surface studies were presented where combination with thermal analysis techniques was possible. One example was taken from organic chemistry where gasification resulted in the production of a reaction interface which could be identified with the surface area as determined from adsorption studies. He cited as a case to be considered the oxidation of carbon blacks. The combination of the two techniques enabled the nature of the active surface to be established. The other example cited was drawn from the decomposition of inorganic materials and in particular the decomposition of lithium oxalate was reported. Here the combination of surface area, thermal analysis and density determinations allowed correct description to be made of the combined sintering and activation behaviour.

Dr. Dollimore pointed out that the design of calorimeters could be quite simple. He described the component necessary for heat of immersion experiments of carbons. Here a Dewar flask and a liquid-in-glass thermometer was the basic equipment necessary to give quite accurate results.

— V. Dondur - Prirodnomatematicki Fakultet - Institut za Fizičku Hemiju - University of Belgrade - Belgrade - Yugoslavia.

Thermodesorption and adsorption calorimetry

The acidity of catalysts is an interesting phenomenon both in view of fundamental research and application of acid catalysts in industrial processes because catalysis of numerous important reactions proceeds at acidic active centers. Several experimental methods have been proposed in order to characterize the acid sites. The main problem is the difficulty of comparing results which were obtained with different methods.

The thermodesorption and adsorption calorimetry of basic probe molecules can be combined in the study of the strength and distribution of acid sites.

A widely used technique to characterize the acidity of zeolites is the temperature-programmed desorption of basic probe molecules. Since the desorption spectra are often poorly resolved it is necessary to employ a curve deconvolution technique. On the basis of deconvoluted desorption spectra the various types of acid sites can be assigned to each desorption peak. The evaluation of desorption spectra provides the kinetic parameters of each particular type of site, the population of respective sites, the desorption rates as a function of the activation energies of desorption and finally the probability function of the activation energies.

The overall heat of desorption can be calculated from the obtained activation energies and populations of the sites. The calculated heat of desorption can be plotted as a function of the degree of coverage.

Another method which is successfully applied in some cases is the determination of the overall acidity distribution by calorimetric measurements of the differential heat of adsorption when acid sites are equilibrated with basic probe molecules.

The measured differential heat of adsorption can be compared with the calculated heat of desorption.

The acidity of dealuminated hydrogen mordenites has been tested in this way. The calculated differential heats of desorption are in good agreement with the experimentally measured heat of adsorption.

— F. Di Renzo - Ecole Nationale Superieure de Chimie de Montpellier, C.N.R.S.
Montpellier - France

TG-DTA in catalyst preparation

The main application in catalysis of the two conventional temperature-programmed thermal methods lies in the study of the catalyst as a solid. Under this aspect TG and DTA are routine techniques, applied to catalysts in all stages of their life, from preparation to aging and regeneration. Indeed they represent quick and cheap techniques, able to give information which by means of other kind of analysis would require more time and be more expensive.

Moreover, they sometimes are the only reliable techniques when other methods fail (e.g. for the quantitative analysis of a multicomponent system including amorphous phases).

Layman use of these techniques is based on the identification of phases by comparison of the temperature of experimental phenomena with standard patterns. For purposes of identification the comparison between analysis carried out in different atmospheres is a very important tool. The detection of undesired phases is the first goal achieved. The second one is the quantitative evaluation of the identified phenomena, especially by TG measurements.

Many examples are possible, including the evaluation of
a) oxides present, through their loss of weight in reducing conditions;
b) supported metals, through the increase of weight in oxidizing conditions;

c) carbonates present, by comparison of the loss of weight in CO_2 with other atmospheres;

d) template in zeolites, giving information both on its amount and its linkage to the lattice.

— L. Lietti - Dipartimento di Chimica Industriale "G. Natta"
Politecnico di Milano, Italy

The use of TPSR (Temperature Programmed Surface Reaction)

The temperature programmed surface reaction (TPSR) technique is usually referred to as a TPD experiment in which the desorbed species is not produced by simple desorption of the initially adsorbed molecules, but originates from surface catalyzed decomposition of the adsorbate, or reaction between co-adsorbates. If suitable operating conditions and probe molecules are selected, intermediate species can in principle be desorbed and detected as soon as they are formed. Thus, valuable information on the nature of intermediate species and surface reactivity can be extracted from the desorption spectra of the products desorbed upon decomposition or surface reaction of the adsorbate, making this technique very attractive for mechanistic investigations. In such a case attention is focused on the reactivity and on the chemical functions of the catalyst surface towards different reactants, rather than on the kinetics of the single desorbed species.

As an example of application of this technique, the TPSR method has been applied to assess the reactivity of a mixed Zn-Cr oxide surface towards linear C_4 aldehyde, alcohol and acid molecules. The results indicate that molecularly adsorbed aldehyde, C4 alkoxide and C_4 carboxylate species are formed at the surface together with the corresponding C_8 intermediates, originating from the aldol-like condensation of two linear C_4 aldehyde molecules. The functions of the surface of the mixed Zn-Cr oxide involved in the desorption upon decomposition or reaction of the above intermediate have been identified, including aldol-like condensation, hydrogenation-dehydrogenation, dehydration, decarboxylation, isomerization and cracking.

— A Vaccari - Dipartimento di Chimica Industriale e dei Materiali,
Università di Bologna - Italy

Temperature programmed desorption (TPD) and temperature programmed reduction (TPR) as a tool for catalyst investigation

Catalysts are difficult to investigate by one technique only on account of their complexity: in fact they present complex chemical composition and/or physical heterogeneity, and are generally defective solids with low or no crystallinity.

Further complications arise from the fact that in catalytic reactions various molecules are involved and reactions generally take place in several steps (i.e. involving active sites of different nature). Moreover the experimental conditions are different from those employed in various surface analysis.

It is thus necessary to employ many different techniques in the study of the structure and reactivity of catalytic systems. Thermal analysis techniques are very useful in catalyst investigation: in particular TPD is able to give information on the nature of the active sites involved in the reaction, whereas by

TPR it is possible to investigate the activation by reduction, a step that may qualify the performances of many metal containing catalysts.

A possible example is the study of the Zn/Cr and Cu/Co/Zn/Cr oxide systems. In the first case, combining the measurement of the heat of adsorption of CO, FTIR spectroscopy investigations and TPD of methanol, the role of Cr^{3+} ions and Zn^{2+} excess ions were revealed. In the second case, the use of TPD of methanol and FT-IR allowed us to interpret the poisoning effect of a small amount of cobalt on classical methanol catalysts. Finally the importance of TPR data was illustrated taking into account the reduction step of catalysts for methanol or methanol-higher alcohol synthesis.