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THE ROLE OF THERMAL ANALYSIS AND CALORIMETRY IN THE STUDY OF POROUS OR DIVIDED MATERIALS

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ABSTRACT

This paper reviews a number of specific applications of thermal methods for the *preparation* and *characterization* of porous or divided materials such as adsorbents, catalysts, fillers or clays.

Special attention is brought to the present possibilities of the three following techniques in the study of the above materials : Controlled Transformation Rate Thermal Analysis, Immersion microcalorimetry and Adsorption microcalorimetry.

INTRODUCTION

The porous or divided materials we are dealing with have grain sizes or voids ranging from the molecular size (a few Å) to the directly visible size (a fraction of a mm). Some of them are *model materials* (like graphite or molecular sieves), but most of them are of a *high technological interest*, as adsorbents (for gas or liquid retention, separation or purification), catalysts, pigments, fillers (in plastics, resins and rubbers) or building materials (cements, plasters, fired clay ...).

We shall first consider their thermal preparation (mainly involving of course thermal analysis) and their characterization (which is more the field of calorimetry).

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THE ROLE OF THERMAL ANALYSIS IN THE *PREPARATION* OF POROUS OR DIVIDED SOLIDS

Using Thermal Analysis *to change the porosity or extent of division of solids*

Many hydroxides, carbonates, nitrates, oxalates, silico-aluminates (natural, like clays, or precipitated) and organic polymers give rise to porous products under the effect of heating.

Nevertheless, to be here fully useful, thermal analysis must allow to control closely the conditions of the transformation and therefore the properties of the final product. At first sight, these are easy to define, since they only involve the changes in temperature and atmosphere *vs* time and since, to make things simpler (both from the experimental and theoretical point of view) we tend to speak (and to think) of *the* temperature of the sample and of *the* composition of the atmosphere surrounding the sample. However, in reality, temperature differences of several K (and sometimes larger than 10 K, as in a number of examples quoted in Liptay's Atlas of Thermoanalytical curves (1)) and partial pressure differences of up to several hundred mbars are observed within the sample submitted to thermal analysis. Assuming that these temperature and atmosphere spatial distributions may be neglected and replaced by a single (and not necessarily "mean") value results in a large loss of information about the mechanism of transformation studied and in great difficulties when a scaling up has to be devised. One may think of several ways to solve this problem :

(a) Either by measuring the temperature and partial pressures at any point of the reacting interface, during its displacement throughout the sample (cf. Fig. 1). However, this is practically impossible.

(b) Either by calculating these parameters from a knowledge of thermal

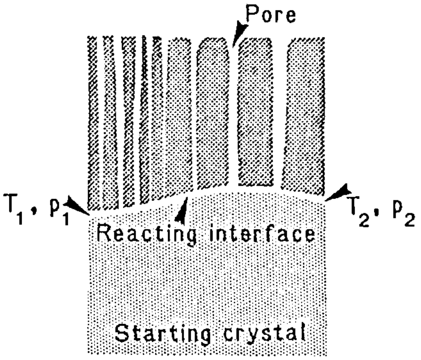

Fig. 1. The nature of the porous products essentially depends on the temperature and partial pressure at each point of the reacting interface.

diffusion and gas diffusion laws. Unfortunately, this needs a previous knowledge of (or a number of assumptions about) the diffusion properties of the sample and product at the various stages of the transformation, so that this approach does not bring really new or reliable information about the system under study.

(c) Either by carrying out the experiment in such a way that these parameters virtually have the same value all over the reacting interface, so that one measurement of each parameter is enough to define the whole system. This is easily done by Controlled Transformation Rate Thermal Analysis, *where the heating of the sample is not controlled to follow a temperature programme but to follow a transformation programme*. The extent of transformation is known simply (and used, at any time, as the controlling parameter) from the quantity which is being measured by the Thermal Analysis device in use : a mass, a gas flow, a heat flow, a length, etc... Controlling the rate of transformation allows to control the temperature and pressure gradients and to keep them at a negligible value. A few versions of this method are described in (2).

Fig. 2 shows a curve obtained by Controlled Transformation Rate Evolved Gas Detection in the case of an α-Be(OH)$_2$ sample. The quite vertical step AB (which is impossible to obtain by conventional TG) corresponds to the homogeneous formation of microporous beryllia (pore width $<$ 1 nm) still partly hydrated, whereas the subsequent parts correspond to a collective increase of these pores to a final width of *ca*. 7.6 nm (3). Not only the mechanism of formation of the pores may be followed and understood, as in the case of alumina (4), but one may prepare the oxide at any "tailor-made" pore size, depending on the application. The temperatures on the recording of Fig. 2 are those at which the porous structure was determined.

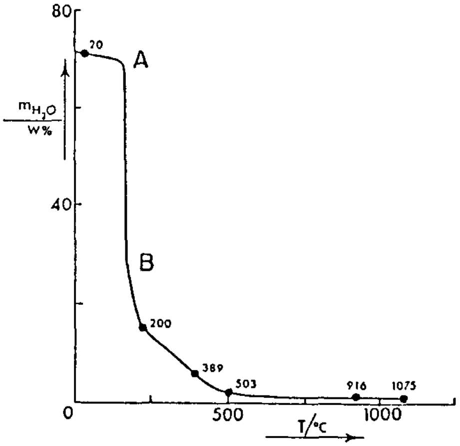

Fig. 2. Controlled Transformation Rate EGA curve of α-Be(OH)$_2$. Outgassing rate : 11.2 mg lost per hour and per g of starting sample.

Using Thermal Analysis *to bring the surface to a reproducible and well defined state*

It is not realistic to bring the surface of a technological adsorbent (i.e. an activated carbon, or silica or alumina) to a "perfectly clean" state, since sintering will often have occurred before. Nevertheless, a well-defined reference state is a prerequisite for a meaningful characterization of these oxides. The selection of the outgassing conditions leading to this reference state may be done with the help of either vacuum TG or Controlled Transformation Rate EGD, as was done for the characterization of a set of reference adsorbents (5), in such a way that (i) the sample mainly loses physisorbed species and that (ii) small variations in the final outgassing temperature only lead to minor changes in the surface. This usually occurs, for inorganic adsorbents, somewhere between 100 and 200°C, in a region of inflexion of the TG curve, corresponding to a lowering of the rate of outgassing just before the desorption of the chemisorbed species.

THE ROLE OF CALORIMETRY IN THE *CHARACTERIZATION* OF POROUS OR DIVIDED SOLIDS

Using DSC to study the *thermal stability* of divided solids

DSC launches the bridge between thermal analysis and calorimetry. It is most useful to study the thermal stability of a divided solid, specially since it allows to distinguish between endothermal and exothermal processes and to detect the first step of a phenomenon which will be detected later -and in some respects too late- by TG or EGA. This is illustrated in Fig. 3 by the DSC curve obtained for the so-called "Ω" or " CS_2-insoluble" sulphur (6) and where we successively observe, when heating at the very slow rate of 2K per hour, in a

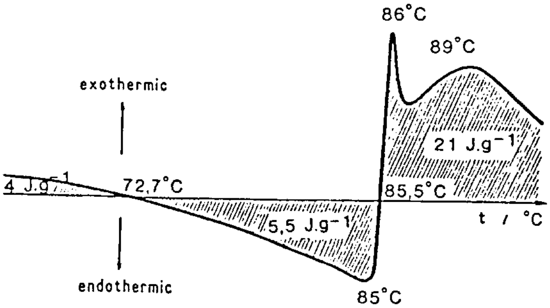

Fig. 3. DSC curve of an Ω-sulphur prepared by vapour condensation on a liquid CS_2 surface.

Tian-Calvet microcalorimeter :

* up to 72.7°C a slight and exothermal transformation into α-sulphur
* between 72.7 and 85.5°C, an endothermal phenomenon corresponding to the rupture of the long helicoïdal chains of Ω sulphur
* between 85.5 and 89°C (final temperature of this experiment) the dominating phenomenon is now exothermal and is likely to correspond to the cyclisation (into octogonal cycles of α-sulphur) of the above fragments.

Using immersion microcalorimetry to determine the *extent, nature and microporosity of the surface*

Provided it is used with a careful closed-system procedure (7), immersion microcalorimetry of a powder into a liquid (most often water, but also an alcohol or an alkane) has been shown to be a sensitive and quantitative way to detect any change on the surface. Pre-coating the surface with an adsorbed multilayer allows to draw the *surface area* from the enthalpy of immersion and from the surface tension of the liquid, by a modified Harkins and Jura procedure (7). Immersing the outgassed surface allows to follow *changes in the hydroxyl density and crystalline structure* of the surface, as seen for instance by immersing in water different silica surfaces, namely a ground quartz, a precipitated silica and a pyrogenic silica. The enthalpies of immersion are 510, 300 and 155 mJ.m^{-2}, respectively, easily explaining a different adsorbing behaviour (8). Also, immersing for instance activated charcoals into different organic liquids (CH_3OH, n-C_3H_7OH, C_6H_6, C_6H_{12}, CCl_4) allows to study the availability of the various sizes of *micropores* (9).

Finally, true hydration reactions may be followed by calorimetry, like those of calcium sulfate (20) or cements.

Using gas adsorption microcalorimetry to study the *structure, homogeneity and microporosity* of the surface

N_2, Ar or Kr adsorption microcalorimetry, specially when associated with quasi-equilibrium adsorption volumetry (10) is a most sensitive way to detect two-dimensional *phase transitions* often occurring at the completion of the monolayer on highly homogeneous surfaces like graphite (11), boron nitride (12) or lamellar halides. When first-order, such a phase transition gives rise to a sharp peak whose height depends on the homogeneity of the surface, as shown in Fig. 4 for the adsorption of Ar on two graphitized carbons. The higher the graphitization temperature, the higher the peak of adsorption enthalpy around $\theta = 1$.

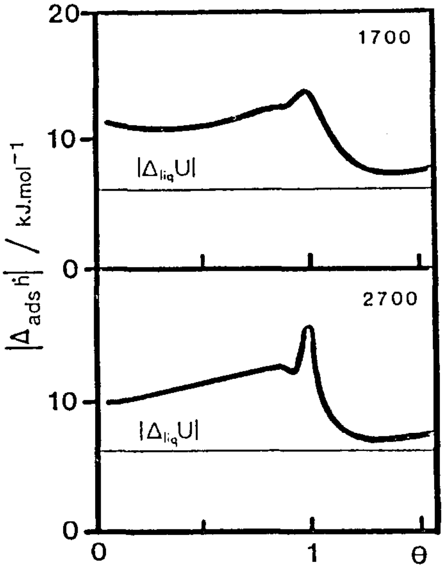

Fig. 4. Derivative enthalpy of adsorption of Ar at 77 K on a carbon graphitized at 1700 or 2700°C.

With the same technique, it is also worthwhile comparing the adsorption of quadrupolar N_2 and non-polar Ar in order to study the chemical or crystallographic state of the adsorbing surface. In that way, one can indeed follow thermally induced modifications such as *changes in the surface hydroxyl density* (in the case of silica) or *formation of cationic metallic sites* (observed for zirconia and titania (13)) which enhance the interactions with N_2 much more than with Ar. Moreover, such a comparison now allows to figure out the proportion of "basal" and "lateral" surface areas in polycrystalline samples like those of kaolinite (14).

Finally, microcalorimetry of chemisorption directly informs about the active sites of the surface (15). The water molecule is a most interesting probe (16) although leading to complicated adsorption systems, whereas H_2, CO, and hydrocarbons are useful to understand the catalytic behaviour and, for instance, a decrease of the catalytic specific activity as the rate of dispersion (of a Pd supported catalyst designed for hydrogenation of the acetylenic bond) increases (17).

Using microcalorimetry of displacement by solutions

This last approach is not at all straightforward and needs a number of different equipments suited for batch or flow-through experiments (18). It then helps to understand the always complicated exchange (often involving the electrical charge of the surface) occurring on the surface between a given number of solute molecules and a different -and usually unknown- number of solvent molecules (19).

REFERENCES

1 "Atlas of Thermoanalytical Curves", G. Liptay ed., Akademiai Kiado, Budapest (1973).

2 J. Rouquerol, in "Thermal Analysis", Academic Press, New-York, 1969, Vol.1, p.281 ; J. Rouquerol, J. Therm. Anal., 2 (1970) 123 ; J. Rouquerol, J. Therm. Anal., 5 (1973) 203 ; J. Rouquerol, Pure and Applied Chemistry, Vol.57, no 1, (1985) pp.69-77.

3 F. Rouquerol, J. Rouquerol and B. Imelik, in "Principles and Applications of Pore Structural Characterization", J.M. Haynes and P. Rossi-Doria Eds., J. W. Arrowsmith, Bristol (1985), pp.213-226.

4 J. Rouquerol and M. Ganteaume, J. Therm. Anal., 11 (1977) 201.

5 F. Rouquerol, J. Rouquerol, G. Thevand and M. Triaca, Surf. Sci., 162 (1985) 239.

6 M. Discours, Y. Grillet, F. Rouquerol and J. Rouquerol, in Proceedings International Symposium on Elemental Sulphur, Nice, 25-27 March, 1987, V2, pp.781-788.

7 S. Partyka, F. Rouquerol and J. Rouquerol, J. Colloid Interface Sci., 68 (1979) 21.

8 R. Denoyel, F. Rouquerol and J. Rouquerol, in "Fundamentals of Adsorption", A. Liapis Ed., Engineering Foundation, New York and American Institute of Chemical Engineers, (1987) 199-210.

9 Y. Grillet, M. François, M.J. Torralvo, A. Guerrero, T. Siemieniewska, K. Tomkow, J. Kaczmaczyk and A. Albiniak, in "Characterization of Porous Solids", K.K. Unger *et al.*, Eds., Elsevier Science Publ., Amsterdam, (1988) pp.483-490.

10 J. Rouquerol, F. Rouquerol, Y. Grillet and R.J. Ward, in "Characterization of Porous Solids", K.K. Unger *et al.*, Eds., Elsevier Science Publ., Amsterdam, (1988) pp.67-76.

11 Y. Grillet, F. Rouquerol and J. Rouquerol, J. Colloid Interf. Sci., 70 (1979) 239.

12 Y. Grillet and J. Rouquerol, J. Colloid Interf. Sci., 77 (1980) 580.

13 J. Rouquerol, F. Rouquerol, Y. Grillet and M.J. Torralvo in "Fundamentals of Adsorption", A.L. Myers and G. Belfort, Eds., Engineering Foundation, (1984)

501.

14 J.M. Cases, P. Cunin, Y. Grillet, C. Poinsignon and J. Yvon, Clay Minerals, 21 (1986) 55.

15 P.C. Gravelle, Thermochim. Acta, 96 (1985) 365.

16 G. Della Gatta, Thermochim. Acta, 96 (1985) 349.

17 A. Guerrero, M. Reading, Y. Grillet, J. Rouquerol, J.P. Boitiaux and J. Cosyns, Proceedings of 4th International Symposium on Small Particles and Inorganic Clusters", Aix-en-Provence,4-8 July, 1988, Atoms, Molecules and Clusters, in press, 1988.

18 R. Denoyel, F. Rouquerol and J. Rouquerol, Colloids and Surfaces, in press (Proceedings International Symposium on Adsorption, Kyoto, Japan, 13-15 June 1988).

19 R. Denoyel, F. Rouquerol and J. Rouquerol, in "Adsorption from Solution", C. Rochester, Ed., Academic Press, London (1982).

20 E. Karmazsin and M. Murat, Cement and Concrete Research, 8 (1978) pp.553-558.