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ON SOME THERMODYNAMIC AND KINETIC ASPECTS OF DESORPTION FROM ZEOLITES UNDER MICROWAVE IRRADIATION

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SUMMARY

The desorption of 13x zeolite is studied under controlled pressure and temperature conditions (T = 42°C) in an apparatus combining microthermogravimetry with a microwave guide ; the experimental study leads to the kinetic and thermodynamic characteristics of the zeolite in the microwave field. The lack of any modifications to the kinetic regime due to the field and some experimental results (evolution of the diffusion coefficient with the microwave power) tends to indicate that the irradiation effect may be reduced in this case to calorific effect.

INTRODUCTION

The first oil-crisis of 1973 has produced in all the world a vast effort of investigation for the use of renewable energies, with the solar energy in the lead. If this solar energy makes up an enormous reserve, its use faces a lot of problems. First, it is necessary to set up the techniques which allow to capture this dilute, uncertain and intermittent energy and then to transform it for storing it. Finally, it is necessary to be able to restore this energy in order to use it.

For all these problems, chemists have solution to offer. They propose chemical compounds "(ref. 1)" which can store and carry solar energy in so-called chemical heat pumps "(refs. 2-3)". These storage proceedings present on electricity the enormous advantage of being able to store and restore energy at will. They use thermodynamic cycles of liquid absorption or solid adsorption. Their applications are designed for cooling, heating and energy storage on a household or industrial scale. But some problems need to be solved for obtaining a better efficiency :

1) The formation problem or more precisely the hydration of an anhydrous adsorbent. It's an essential stage of chemical cycling.

2) The problem of regeneration which is often performed by pumping or by conventional heating which present a lot of major drawbacks. It's a long and difficult operation which always requires high temperatures.

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In both cases, the knowledge of the transformation requires either :

* A basic or fundamental study, for example, the knowledge of reaction mechanisms in the hydration case or the research of microwave field effect applied to a material during the regeneration (specific effect or heating).

** Or applied study of research on key parameters of the real working of these systems. For example, the mass effects, the dehydration-hydration cycle effects, the delay time or other parameters as the power of the field or pressure of adsorbent gas.

In this paper, we will devote our attention to only one of these points :the research of microwave field effect applied to a material during regeneration.

We will focus our attention on the microwave action, because at present, they constitute new and fruitful means of investigation "(refs. 4-10)" such as drying, lyophilisation, thawing or dehydration. Indeed it's a means of carrying and dissipating energy everywhere, in volume or at interfaces.

The aim of this study is to supply the relevant elements to answer the following questions :

(i) Is microwave interaction a simple conventional heat or is there a specific action of the field ?

(ii) How do the kinetics of the regeneration stage evolve in the presence of microwave power ?

(iii) What are the working parameters (Pressure P, temperature T and power π_i) of an affinity thermal machine using 13x zeolites as adsorbent ?

EXPERIMENTAL

The apparatus is composed of three essential parts :

- The microwave guide
- The thermobalance
- The reactor.

Microwave

The microwave part (Fig. 1a) is made up of a wave generator (1), operating at a frequency of 2,450 MHz and protected by a wave circulator (2). The reflected power is diverted towards an adapted water load (3). The generator supplies a rectangular wave guide (4) (type RG 112/U) inside which a progressive wave is propagated. The transmitted power is absorbed by a second water load (5).

Thermobalance

The coupling of both methods-microthermogravimetry and microwaves-(Fig. 1a) carried out in laboratory allows to record continuously under controlled pressure and temperature, the variations of mass of irradiated samples using

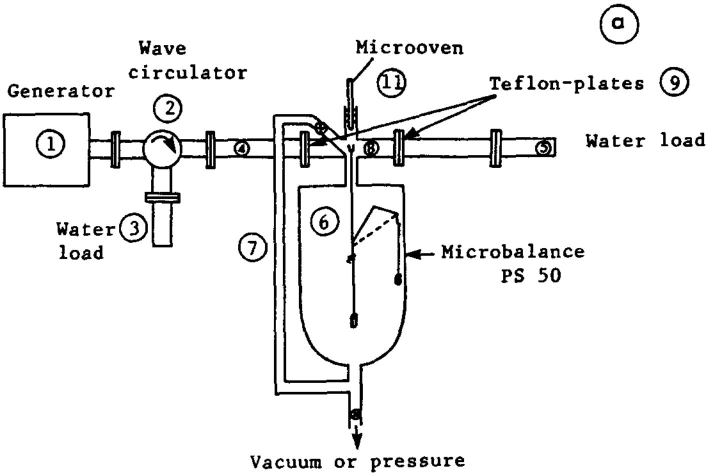

Fig. 1a. Experimental Apparatus : microwave circuit.

a microbalance (6) of zero SETARAM type PS 50. It's a dissymetric balance, its sensitivity is 1/50 g. This apparatus of maximum load 50 g is currently used through its possibilities of electromagnetic taring if we often vary the mass sample. It is positioned under the wave guide and connected with the reactor by a metallic tube (7) in order to avoid overpressures at the level of the scoop (8).

Reactor

The reactor (Fig. 1b) consists of a part of wave guide, closed at its extremities by two teflon-plates (9) which are 4 mm thick, its temperature is fixed by means of a furnace ribbon piloted in power by a rheostat. The guide has a hole at the centre of its larger faces to let the sample-stand pass. This one is made up of a quartz-stick of 2 mm diameter and supported by one of the beam branches and allows to position the sample in a wave guide axle. The tightness of the reactor is provided by toric joints (10).

The reactor is topped by a microoven (11) consisting of a cylindrical spooling (12) made from a heating element with cold extremities type THERMOCOAX. The tightness to vacuum and to pressure is provided by the utilization of tight crossing mounted on a brass block, which slides via toric joints in a cylindrical tube. This microoven is necessary for the previous activation of 13X zeolites.

Procedure

After activation of 13X zeolite in temperature T = 350°C and pressure = vacuum, conditions during 24 hours, we rehydrate it by imposing through the cold point, a water vapour pressure corresponding to the saturation of zeolite at temperature (T = 42°C). From this hydration state, the dehydration is achieved

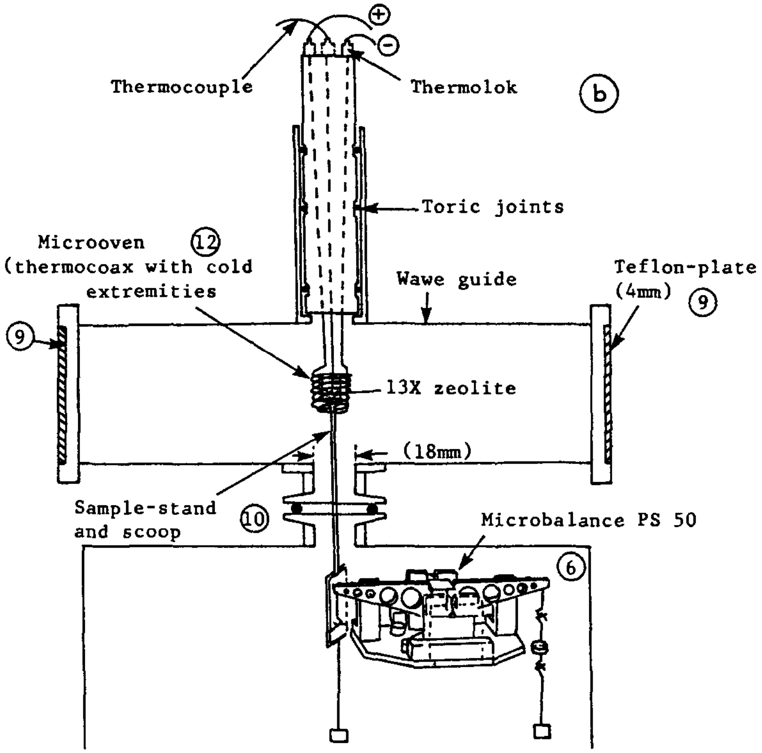

Fig. 1b. Expérimental Apparatus : microwave-thermogravimetry coupling.

for a given pressure in a 0.1 - 4.5 kPa range in accordance with incidental power π_i. It must be noted that after each dehydration, the sample is rehydrated again, always in the same conditions (T = 42°C, P = 5.6 kPa and π_i = 0W).

RESULTS

The desorption curves

The action of the microwave field on the dehydration of 13X zeolite is shown by the thermogravimetric curves (Fig. 2) representing the evolution

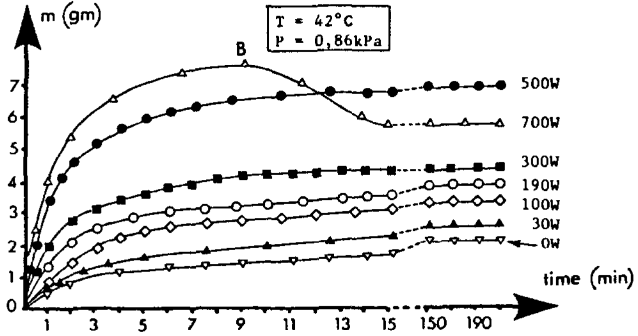

Fig. 2. Example of loss-mass curves m versus time, T = 42°C and variable powers.

of the desorbed water mass versus time, at a constant water vapour pressure and for different powers π_i. From these curves, different observations can be made.

1) At null field and whatever the pressure, the m(t) curves have a quasi-parabolic shape. In the presence of microwave field, we observe an evolution of the shape of curves which then presents two parts :

(i) First, an initial fast rise, corresponding to a loss of mass with a speed all the more important since the power is high. This first part lines up with the following expression :

$$\alpha = K\sqrt{t} \quad \text{(Fig. 3a)} \quad \text{"(ref. 11)"}$$

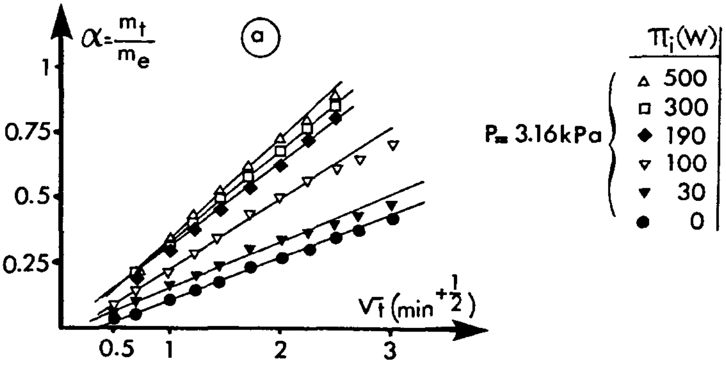

Fig. 3a. Linear transform of experimantal curves m(t) : $\alpha = K\sqrt{t}$ law (short time).

(ii) The second part of the curves corresponds to a continuously decreasing speed until reaching a stage in the chosen pressure P, temperature T and power π_i conditions. This one lines up with the following expression :

$$Ln(1-\alpha) = K' + K''t \quad \text{(Fig. 3b)} \quad \text{"(ref. 11)"}$$

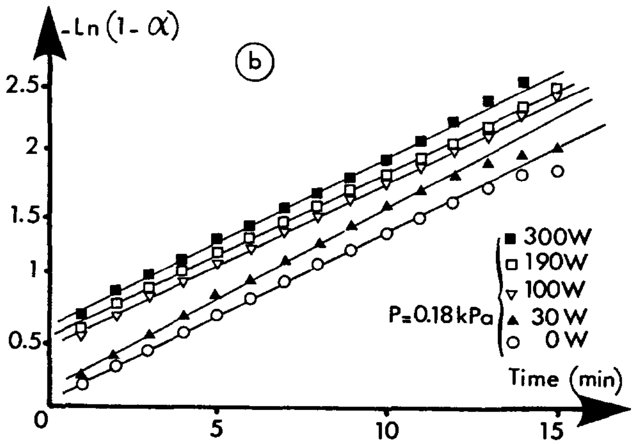

Fig. 3b. Linear transform of experimental curves m(t) : $ln(1-\alpha) = K' + K''t$ law (long time).

Then, we can notice in this case, that the curves obtained in field are interpreted with the same laws as those in null field. There are no alterations of kinetic system through the application of an electric field.

2) For higher powers (π_i > 500 W) and in particular for the weaker pressure values, other curves are obtained as you can see in Fig. 2 (curve B). After a first part which seems to be the same, the loss of mass reaches a maximum, and then goes through a stage which represents a rate of hydration slightly smaller than that previously hoped for the given power, while such curves at slight pressure and high powers are obtained a microwave plasma is produced in the reactor.

3) The general shape of the curves, with continuously decreasing slope, present a maximum speed of desorption (v_o) at the time origin and it always reaches a decomposition step (m_e). We notice that as far as the limit value of the experiment (π_i = 500 W), the curves v_o $(\pi_i)_p$ and m_e (π_i) are linear.

The desorption equilibrium under field

The influence of the field over the desorption equilibrium is shown in figure 4 , which represents the network of the isotherm curves $M = f(P)_T$ obtai-

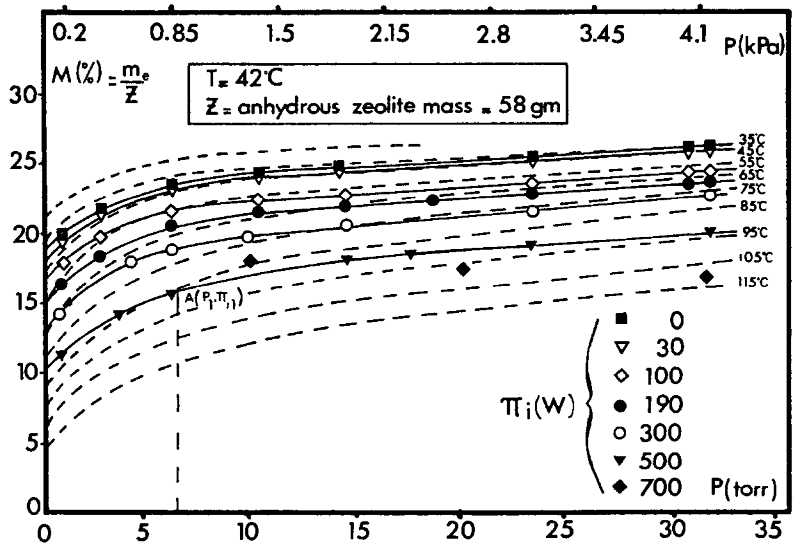

Fig. 4. Network of adsorption isotherms calc. "(refs. 11-12)" and isopower curves.

ned by calculation "(refs. 12-13)". The compositions obtained with various pressures and values of the power (isopower curves) can be plotted on the same graph . It is experimentally checked that the equilibrium desorption obtained for P_1 and π_{i1} values of pressure and microwave power (point A in the figure 4) is the same as the equilibrium obtained under the same pressure P_1 at a temperature T defined by the junction of the considered isopower curve and the isotherm which goes through point A.

The desorption equilibrium obtained in field appears as a result of the heating of the zeolite by the field, because of the steady temperature obtained by the application of the latter. The quantity of adsorbed water at the desorption equilibrium depends on the power of the field through the material temperature imposed by the field.

Evolution of the diffusion coefficients with the power of the field

The appropriate transformation $\alpha = f(t)$ (Fig. 3) enable to reach the water diffusion coefficient in the zeolite. Their evolution is represented as a function of the microwave power in (figure 5a). This figure invites two remarks :

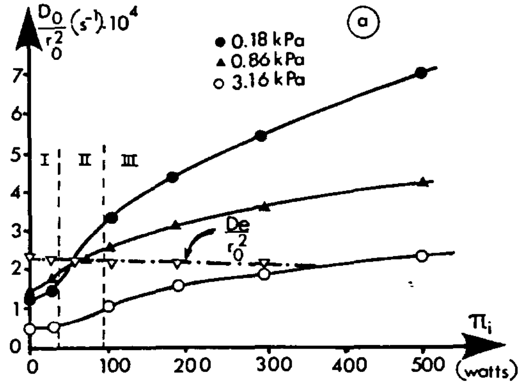

Fig. 5a. Variation as function of the incident power of : the diffusion coefficients.

(i) We notice that D_e coefficient which characterizes the diffusion of water in near conditions to the thermodynamic equilibrium varies little with the power of the field.

(ii) We observe that D_0, the coefficient characterizing the diffusion of water in conditions far removed from this same equilibrium, increases with the field, at constant pressure. This result can lead to infer an evolution of the diffusion coefficient with the field and the opportunity of a specific action of the field on the material.

Infact, the comparison between the curves of the figure 5a, and those obtained for the temperature (Fig. 5b) shows that both offer three parts corresponding to three domains of power.

(iii) A first part I, is at $\pi_i < 30$ W power in which the effect of the field is negligible.

(iv) For $30 < \pi_i < 100$ (part II), the temperature follows a linear variation depending on the power, the slope depends on the pressure.

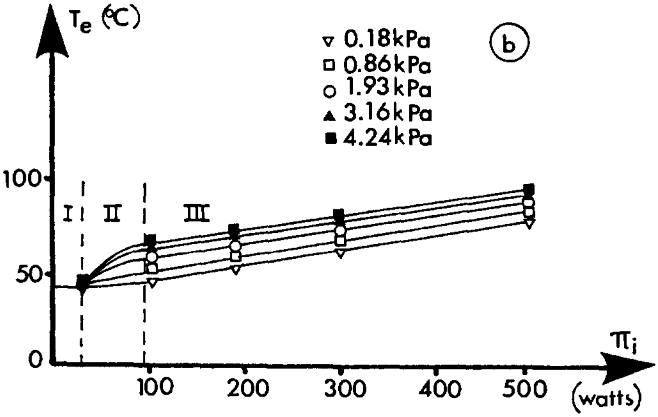

Fig. 5b. Variation as function of the incident power of : the material temperature at the desorption equilibrium.

(v) If π_i > 100 W, the zeolite temperature varies proportionally to the power, but the slope keeps independent of the pressure (part III).

INTERPRETATION

These results can be interpreted by taking into account the fact that the incident power is divided into three parts.

(i) The power used for the heating of the zeolite which justifies an increase of the temperature of this material.

(ii) The power used to compensate for the losses after a heat transfer.

(iii) Finally, the power used for the desorption which is a consequence of decrease of the temperature of the zeolite. We notice that this power is below the incident power and adopts a linear variation with the latter in a 1 to 1000 ratio in accordance with that of the sample-guide surfaces.

Thus, at a given pressure and microwave power, a steady state of the irradiated material can be reached if the processes leading to a possible cooling down, chiefly desorption, are compensated by the heating term.

Then, if we consider this division of the incident power, we will understand the variation of the obtained curves (Fig. 5).

1) At low power (part I of the curves) during the desorption, the temperature of the zeolite is practically the same as the temperature of the reactor. The desorption phenomenon uses nearly the total power applied on the material Initial and instantaneous speeds increase with the power of the field : speed is regulated by the bringing of energy and not by the pressure.

2) At high powers (part III), we notice that the zeolite gets heated. The bringing of energy is then no longer the factor limiting the desorption ; the maximum speed of desorption is then fixed by a chemical restriction imposed by

local conditions of temperature and pressure. The surplus of microwave energy, which has not been used by the desorption process, is first used to heat the material and then possibly to initiate secondary phenomena (Plasma).

3) At intermediate powers, kinetics of desorption and thermic exchanges have the same participation in the global desorption process.

CONCLUSION

From an experimental apparatus, linking microthermogravimetry with a wave guide, we have carried out a study concerning the 13X zeolite desorption in a field, through a preliminary activation of the zeolite. The experimental investigation has allowed to draw the progression curves in a reproducible way, pointing out the characteristics of such transformation in field. In the concerned field and pressure domain, the study does not seem to take out any specific interaction mechanisms of the field. The results obtained are mostly explainedby the thermic evolution of the material under a microwave field, acting essentially with the supply of calorific energy.

In this case, the systematic experimental study which depends on pressure and power has provided some precisions concerning thermodynamic and kinetic characteristics of the desorption of 13X zeolite in field. This information could be used in parallel connection with that already published and used favourably in the elaboration /implementation of a microwave applicator, conformable to the stage of zeolite regeneration in a machine producing cooling from an adsorbate-adsorbent cycle.

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