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STUDY OF HYDRIDE FORMING SYSTEM BY THERMOGRAVIMETRY. ROLE OF THE SAMPLE MASS IN EXOTHERMIC KINETICS.

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ABSTRACT

In $LaNi_5/H_2$ systems fast exothermic formations exhibit a complex relationship between the reaction rate and the sample mass. A decrease in the reaction rate is particularly observed when the mass is reduced in the range of 30 to 5 mg. It is shown here that heat flow cannot be the regulating step.

INTRODUCTION

Kinetic studies of solid-gas fast exothermic reactions set up the troubling problem of determining if heat accumulation occurs ; and as a consequence if the resulting heat flow can be, in fact, the regulating step which imposes the reaction rate. This artefact has been put forward in the $LaNi_5/H_2$ system (ref. 1) to explain the large differences in the obtained values of the reaction rate : from 0.0831 mn^{-1} (ref. 2) to 30 mn^{-1} in a recent work (ref. 1). An experimental way of precisely stating the preceding point is an investigation of the relationship between reaction rates and sample masses : if the reaction rate is only dependent on a chemical step, it must not be affected by relatively large changes in the sample mass, on the contrary, the heat flow could be one of the parameters involved in a decrease of the reaction rate when the sample mass is increased.

In this paper microthermogravimetry under hydrogen pressure is chosen to reinvestigate the kinetics of the reversible $LaNi_5$ hydride formations according to equation 1 :

$$LaNi_5 + 3H_2 \rightarrow LaNi_5H_6 \quad \Delta Hf = - 30.2Kj/H_2 \qquad (1)$$

APPARATUS SAMPLES AND PROCEDURE

Microthermobalance

The hydrogen high pressure microbalance (0-10MPa) is built from a genuine Setaram MTB 10-8 symmetrical - beam zero microbalance. The limiting accuracy is 1 μg. Mass compensation is by electromagnets and detection in position is carried out by the use of a lamp and photo cells. This modulus is placed in a high

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pressure bell fitted with two laboratory-tubes. The device is as symmetrical as possible (two samples, one of them is inert) and a double symmetrical furnace. Pressure is measured with a Bourdon lab. Manometer, temperature is recorded from a chromel-alumel thermocouple located inside the laboratory tube just beneath the sample holder.

The device can be evacuated in a primary vacuum.

Samples

The $LaNi_5$ alloys have been prepared and characterized at the CNRS rare earth laboratory of Bellevue, France. The bulk is crushed in small pellets and laid in a stainless steel cylinder 10 mm in diameter.

The sample mass ranges from 10 mg to 300 mg ; such a mass corresponds to a layer of approximatly 1.5 mm for the 300 mg and scattered clusters for the 10 mg. The average size of the grains is 5 µm. The hydrogen used is "U" quality from "Air Liquide" which contains, according to the manufacturers, 5 ppm of water vapor and 5 ppm of oxygen.

Hydride formations are carried out, under constant P_{H_2} and imposed temperatures, as a function of time. From the sigmoïdic formation curves the reaction rate is obtained by drawing the tangent when $t = t_{0.5}$ and by calculating the tangent slope. $R_{0.5}$ is expressed in H per second and corresponds to the half reaction rate value.

EXPERIMENTAL RESULTS

Figure 1 gives, as an example, the family of straight lines obtained when the

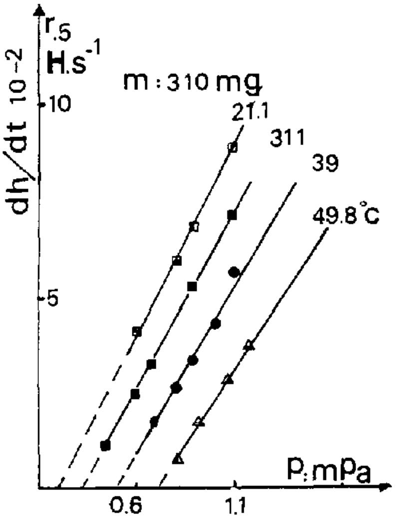

Fig. 1. Reaction rate $R_{0.5}$ versus the hydrogen pressure for four imposed temperatures.

reaction rate is plotted against the pressure for four imposed temperatures. The intersection of these lines with the P_{H_2} axis gives the "equilibrium pressure Pe" whose value is used to calculate ∆P = (P_{H_2} − Pe). ∆P is the actual pressure parameter in the reaction rate equation, such a transposition is shown in figure 2 for a sample masse of 31 mg. In figure 3 the different reaction rates obtained

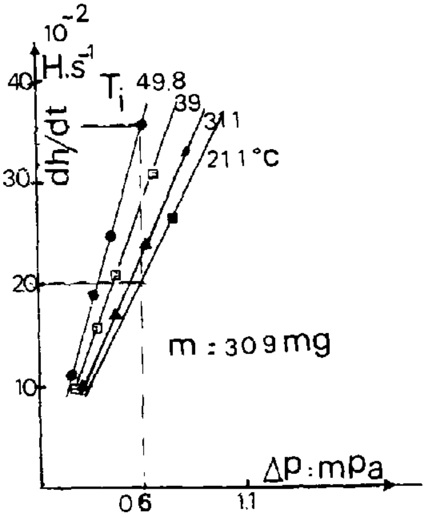

Fig. 2. Reaction rate $R_{0.5}$ as a function of ΔP = (P_{H_2} − Pe).

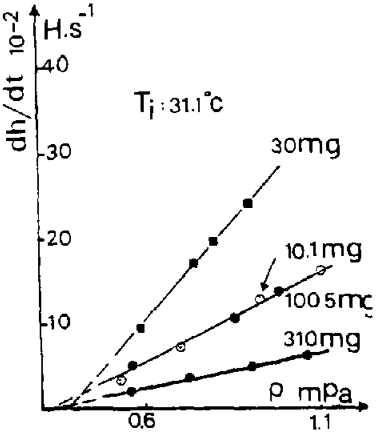

Fig. 3. Reaction rate versus hydrogen pressure as a function of the sample mass.

with four masses under the same conditions are gathered. A synthesis of these results is given in figure 4 which represents the reaction rate change as a function of the sample mass under an imposed temperature of t_i = 21°C and a P_{H_2} of 0.5 MPa. It is to be noted that the reaction rate changes mainly with a change in mass and that this diagram is divided into two parts by a sharp maximum in the reaction rate near a mass of 30 mg. On the left there is a linear decrease in $R_{0.5}$ when the mass is decreased (the slow value of ref. 2 obtained with a mass of 5 mg and marked by a star fits this diagram well). On the right side of the figure there is a decrease in $R_{0.5}$ when the mass in increased.

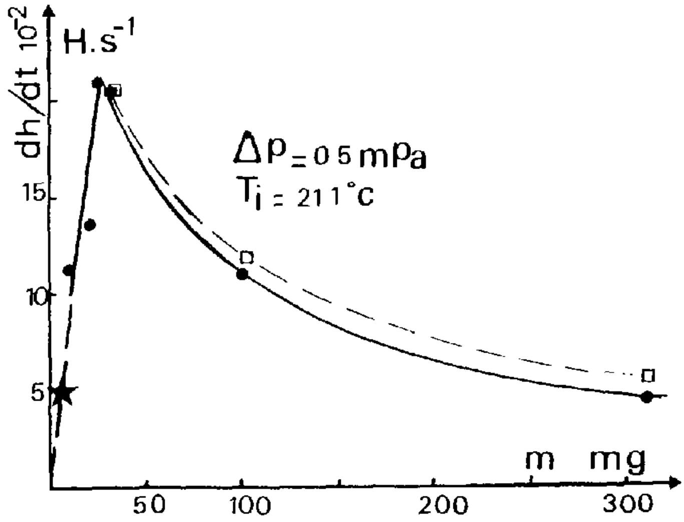

Fig. 4. Reaction rate as a function of sample mass. The value noted by a star has been obtained in ref. 2 with a mass of 5 mg.

To test the part played by heat flow on the preceding results, a series of experiments has been carried out under the same conditions of device, mass of sample, pressure and imposed temperatures but with the thermocouple head inside the powder (the sample holder being disconnected from the beam and placed directly on the thermocouple head). The recorded quantity is $\Delta T = T_a - T_i$ in which ΔT is the difference between the sample temperature T_a and the imposed temperature in the gas T_i. The results are given for the masses of 310 mg and 30.9 mg respectively in figures 5 and 6. It appears that : first a temperature increase ΔT occurs with the reaction, greater for a mass of 310 mg than for a smaller mass ; ΔT decreases when T_i increases from 21.1°C to 50°C. Secondly, such diagrams allow recalculating for each mass and each pressure the actual temperatures T_a wich have to be assign to the preceding experimental reaction rate values.

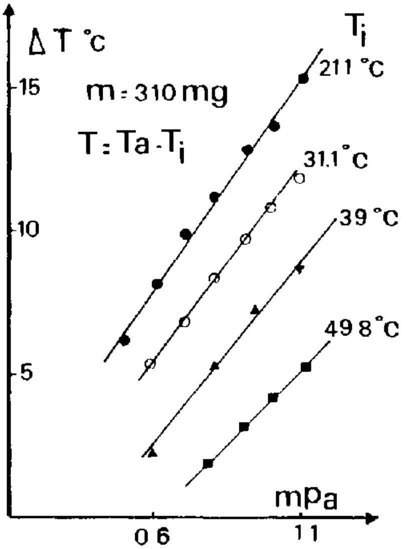

Fig. 5. ΔT : difference between the actual temperature T_a and the imposed temperature T_i as a function of the imposed temperature and of the hydrogen pressure.

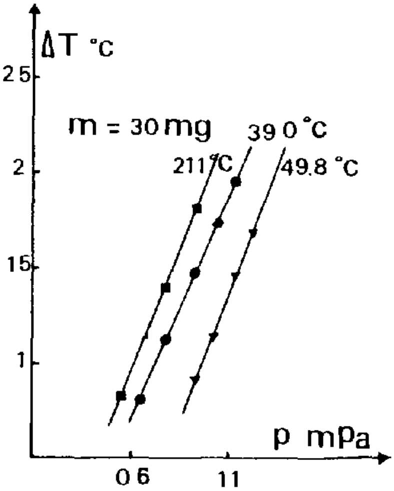

Fig. 6. ΔT : difference between the actual temperature inside the sample and the imposed temperature.

Such new functions in which the reaction rate is plotted as a function T_i and T_a are shown for the two masses in figures 7 and 8. The new functions are deduced from the preceding ones by a translation equal to ΔT. The corrected function $R_{0.5} = f(m)$ which takes into account the heat effect associated with the reaction is represented by a doted line in figure 4. It is evident, that this correc-

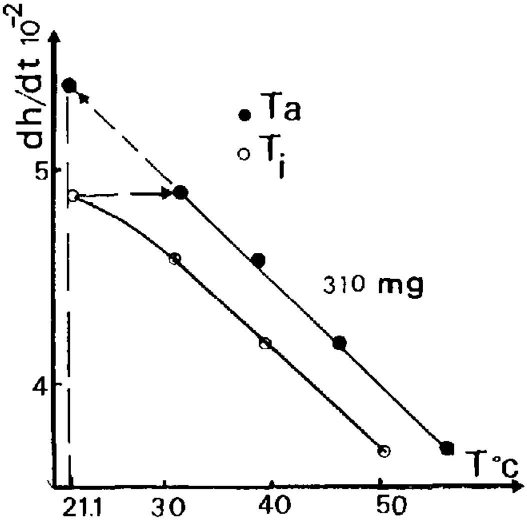

Fig. 7. Reaction rate versus
a) the actual temperature inside the sample
b) the imposed temperature of the gas.

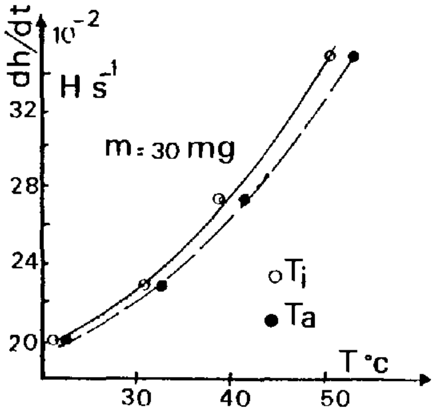

Fig. 8. Reaction rate versus
a) the actual temperature inside the sample
b) the imposed temperature of the gas.

tion does not modify the relationship between the reaction rate and the sample mass. In other words, it does not make $R_{0.5}$ independent of the mass as one could expect it if the heat flow were the regulating step.

CONCLUSIONS

One notices that these exothermic formations induce a heat accumulation during fast reactions. This heat accumulation is expressed by a difference between the temperature inside the sample and the imposed temperature (ΔT varying as the square root of the mass in the explored domain). The resulting heat flow is not the regulating step since all corrections do not restore a reaction rate independent of the sample mass. The most intriguing result is the decrease in reaction rate when the mass is decreased to samples of a few mg. One hypothesis which can be set up in this system, is that if surface reactions play a part in the regulating step as generally admitted in $LaNi_5$ system (ref. 3, 4, 5). When a mass of sample placed in a fixed volume, which contains a number of inhibiting molecules, is reduced for instance by a factor of two ; in fact, it corresponds to an increase, in the same proportion, in the surface of the sample which is inhibited by these impurities, and as a consequence, of the same decrease in the reaction rate.

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