



Reference 2

PICO-CHEMISTRY: A POSSIBLE CLEAN AND ABUNDANT ENERGY

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Abstract

The search for energy sources producing no CO₂, no harmful wastes and available on a large scale, is becoming more and more important: the climate is changing, the oil and gas resources are declining and the long term storage of the by-products from nuclear energy is difficult. The theoretical possibility of new chemical phases, with very high enthalpies of formation, in some hydrogen/metal systems has been evaluated. It was proposed to call these phases pico-hydrides. They might be synthesized from metals such as Nickel or Iron and Hydrogen, in the presence of a catalyst and with the emission of soft X-Rays (energy in the order of magnitude of the energy of the K layer of the metal). The enthalpy of formation of a Nickel or Iron pico-hydride is thus very high (some 800 MJ/mole) and the products of the reaction (pico-hydrides) are likely to be metal-like compounds with possibly interesting properties such as being room temperature super-conductors. Once formed, pico-hydrides emit no radiations.

Keywords: New clean energy source, New metal like compounds, Room temperature super-conductors.

1. Introduction

The interaction of Hydrogen with certain metals able to absorb or adsorb Hydrogen, have been extensively studied, in view of various applications: Hydrogen storage or Hydrogen isotopes separation, production of finely divided Nickel particles, catalysis etc. In [1] the kinetics, energetics and stoichiometries of the adsorption of Hydrogen on supported Nickel have been studied. Values of enthalpies of reversible adsorption up to 123 KJ/moleNi have been measured for Ni supported on silica.

By contrast, in this study, an irreversible adsorption of Hydrogen has been observed when nano size Nickel particles are in contact with substances having a low electron work function (European Patent Application n° 12075001.3). Moreover an enthalpy of adsorption in the order of 400 KJ/moleNi has been measured. This reaction takes place on long periods of time (several days). To explain this type of results, the possibility of new chemical phases (with extremely high enthalpies of formation) in some hydrogen/metal systems has been theoretically evaluated [2].

2. Experimental

2.1. The calorimeter

A simplified type of DSC has been built. The calorimeter has 2 identical cells, longitudinally placed in the 50 mm diameter tube of a horizontal CERADEL heater. The heater temperature is regulated (N type thermocouple). The powder to be studied is placed in one of the cell (the active cell). A calibration resistor is placed in the other cell (the reference cell). Each cell consists of:

- an aluminum tube (40/48 mm ID/OD and 140 mm long) equipped with a PT 100 (in a longitudinal hole bored in the thickness of the tube) that measures the "heater" temperatures T_H of the cell.

- an aluminum cylinder (35 mm OD and 140 mm long) centered inside the aluminum tube and in which are bored two holes: one in the center (10.5 mm diameter) that contains the powder or the calibration resistor and one (6 mm above the first hole), that contains a PT 100 that measures the "reactor" temperatures T_R of the cell.

The powder and the calibration resistor are placed in 2 identical stainless steel cylinders (6/7.5 mm ID/OD and 130 mm long). Each of these cylinders are placed in stainless steel tubes (8/10 mm ID/OD) that were inserted in the 10.5 mm holes bored in the center of the aluminum cylinders. These tubes are connected through a manifold either to a primary vacuum (4.5 Pa) or to a Hydrogen cylinder. The connections to the manifold are by Gyrolock fittings well outside the heater and the extremities of the tubes inside the heater are closed by welded closings: there is thus no possibility of hydrogen leakage inside the heater. The wires of the resistor go inside the 10mm OD tube and reach the DC generator through insulated connections. The whole experimental set-up is installed in a closed and ventilated cabinet. The room where the cabinet is installed is air-conditioned. The drawing of one cell is shown in *Figure 1*.

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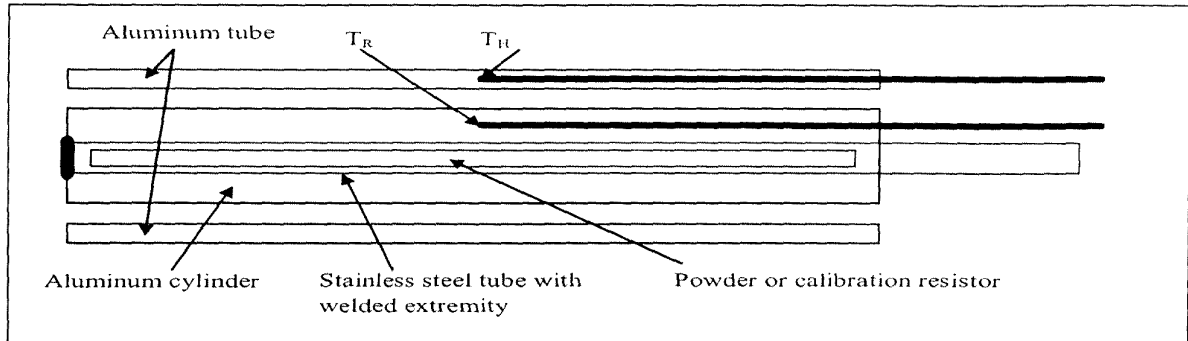


Figure 1 Schematic drawing of one of the 2 cells of the calorimeter

2.2. The principle of the heat fluxes measurement

The heat fluxes from the Ceradel heater flow through the aluminum tubes, the air gap between the aluminum tubes and the aluminum cylinders and then through the 10 mm OD stainless steel tubes and the PT 100 (and the wires of the resistor in the reference cell) of each cell to the air outside the heater. The aluminum thermal conductivity being much higher than the air gap thermal conductivity (230 to be compared to 0.050 W/mK at 50°C), the temperatures T_R and T_H may, in first approximation, be considered as constant in the totality of the aluminum tubes and cylinders. The steady state power W exchanged between the tubes and the cylinders is thus:

$$W = K * (T_R - T_H) \quad (1)$$

K (W/K) being an experimentally measured coefficient that takes into account the heat exchanged between the cell and the air outside the heater through the 10mm OD stainless steel tube and the PT 100 (and the resistor wires).

When a perturbation dW occurs during time dt in the reactor of a cell (reaction or calibration), the additional heat increases (or decreases) the temperature T_R of the cell inducing a variation of the heat exchanged with the tube. Thus:

$$dW dt = MC dT_R + K * (T_R - T_H) dt \quad (2)$$

M being the mass of the aluminum cylinder and its internals and C their average heat capacities (in first approximation, T_H is constant because the heater temperature is regulated).

If the 2 cells were absolutely identical the differential temperatures $(T_R - T_H)_{ACT}$ and $(T_R - T_H)_{REF}$ would be equal before the perturbation giving the net additional heat flux due to a perturbation in the active cell:

$$dW dt = (MC) * (dT_R)_{ACT} + K * [(T_R - T_H)_{ACT} - (T_R - T_H)_{REF}] dt \quad (3)$$

In the real set-up, $(T_R - T_H)_{ACT}$ and $(T_R - T_H)_{REF}$ are slightly different (resistor wires). Moreover, the effect studied lasts on long periods of time (several days): the drifts of the differential temperatures, that are slightly different, have to be taken into account. The strategy used to extract the thermal signal from the raw data was to first correct the temperature drifts (linear correction) and then to normalized the active cell temperature difference against the reference one. A detailed example of such an approach is given below. This approach also takes into account the successive use of vacuum and Hydrogen pressure in the system.

Prior to the experiments, a relative calibration of the 4 PT 100 was run over the temperature range 25 to 550°C, yielding a linear relative correction (the reactor temperature of the active cell was chosen as the reference). Also during the experiments, calibrations of the system are run under hydrogen pressure (8 bar, regulated and measured) by injecting a given amount of electrical energy in the reference cell (DC current). At 450°C (using (3) and its integer) the water equivalent of the cell was found to be 480 J/°C, in line with the cell physical characteristics ($M=560g$) and the time constant (upon cooling and fitting the cooling curve with an exponential) was found to be $\tau_e = 850s$. The experimentally measured time constant τ_e is lower than would result if the aluminum cylinder of a cell did not exchange with the air of the cabinet: the time constant τ resulting from (2), would then be $\tau = MCe/\lambda S = 2800 s$, with e being the thickness of the air gap, S its surface and λ its thermal conductivity (in that case, $K = \lambda S/e = 0.17 W/°C$).

During an experiment, the temperatures T_H and T_R of the active and reference cells and the air temperature of the cabinet T_A are monitored every 2 minutes with a data logger. A spread sheet is used to visualize the evolution of the air temperature and of the temperatures differences of the 2 cells with time. Using (3), the evolution of the instant power with time is calculated (together with the cumulated energy production with time, which is the integer of (3)).

2.3. Preparation of the Nickel containing powder

3.82 g of Nickel oxide nano-particles (US Research Nanomaterial - NiO 99% -10/20 nm) and 3 g of Lanthanum Hexaboride (LaB₆ Alfa Aesar - 99,5% - <325 Mesh) were dispersed in 500 cm³ of water (ultra-sound 5 times 7 minutes). 4 g of a fresh precipitate of Calcium carbonate was prepared from Calcium nitrate and Sodium carbonate. The precipitate was decanted and washed 3 times and was then poured into the dispersion of NiO and LaB₆, while mixing at 3500 rpm during 5 minutes. The mixture was decanted and washed 3 times with 500 cm³ of water and filtered. The final precipitate was washed 3 times with acetone. After evaporation at ambient of the acetone, the solid mixture was heated overnight at 80°C and crushed (<500 µ).

3.81 g of the powder (2013-11-08-precu) were then loaded in the 7.5 mm OD stainless steel tube of the active cell. The composition of the powder is given in **Table 1** below.

Table 1. Composition of the powder 2013-11-08-precu (%Weight)

CO ₃ Ca	40
NiO	30
LaB ₆	30

3. Description of the experiments

After loading of the powder, the experimental set-up is installed in the cabinet and connected to the manifold. The regulated temperature of the heater is then set at 350°C and the reactors are submitted to a vacuum of 4.5 Pa, at 350°C during one night. This activates the powder and yields the base line under vacuum at 350° C. Without dismantling the experimental set-up, following experiments are then run (See summary in **Table 2** below).

3.1. Reduction of the Nickel oxide (experiment 2013-12-15)

The Nickel oxide in the activated powder is reduced by submitting it at 350°C to a hydrogen pressure of 8 bars during half an hour and then submitting it at this temperature to a vacuum of 4.5 Pa during 12 hours (overnight). This cycle is repeated 3 times. The amount of reduced Nickel under experiment is thus 1.05 g.

3.2. Run at 455°C (experiment 2013-12-19)

After NiO reduction, the regulated heater temperature is set at 455°C and the system is left overnight under a vacuum of 4.5 Pa, yielding the initial base line under vacuum. At t= 20000 s Hydrogen is admitted in the cells reactors at a pressure of 8 bar. At t=45000s, a calibration is run by injecting 25 mW during 3600 s in the reference cell (DC, 90 J). At t=265000 s, the hydrogen is evacuated and the cells are submitted overnight to a vacuum of 4.5 Pa, restoring the base line under vacuum.

3.3. Run at 550°C (experiment 2013-12-26)

After the experiment at 455°C, the heater temperature is set at 550°C and left overnight under a vacuum of 4.5 Pa. At t= 40 000s hydrogen is injected into the cells reactors at 8 bar. At t = 208000 s a calibration is run by injecting 25 mW during 3600s in the reference cell (DC 90J). At t=282000 s, the hydrogen is evacuated and the cells are submitted overnight to a vacuum of 4.5 Pa, restoring the base line under vacuum. See **table 2** for durations.

Table 2. Duration of the experiments

NiO reduction	1.5 hour
Run at 455°C	68 hours
Run at 555°C	67 hours

4. Processing of the data.

The strategy used to extract the thermal signal from the raw data will be given in details for the experiment at 455°C (2013-12-19). The final results will then be given for the 2 other experiments.

4.1. Run at 455°C (experiment 2013-12-19)

When Hydrogen is introduced in the cells, an additional temperature drop is observed in the reactors, due to the presence of the gas. In the range of pressures used, the thermal conductivity of a gas does not depend upon the pressure (this is a direct consequence of the kinetic theory of gases – see Sutherland formula). In any case, the hydrogen pressure is the same in both cells.

Figures 2 and 2' show the evolution with time of $(T_R - T_H)_{ACT}$ and $(T_R - T_H)_{REF}$. It is obvious at first glance that these temperature differences are not exactly equal for both cells. It is observed that $(T_R - T_H)_{ACT}$ is always lower than $(T_R - T_H)_{REF}$ (calibrating resistor wires). Moreover, the drift with time for both cells (measured under a vacuum of 4.5 Pa, before and after hydrogen introduction), is different: $6.8 \cdot 10^{-7} \text{ } ^\circ\text{C s}^{-1}$ and $8.2 \cdot 10^{-7} \text{ } ^\circ\text{C s}^{-1}$ for the active and reference cell respectively. Running averages on 15 periods of two minutes are indicated on the figures.

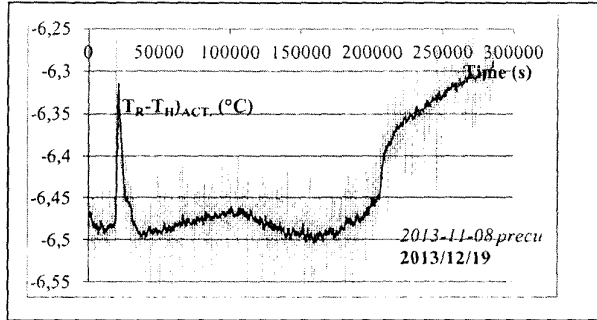


Figure 2 Evolution with time of $(T_R - T_H)_{ACT}$

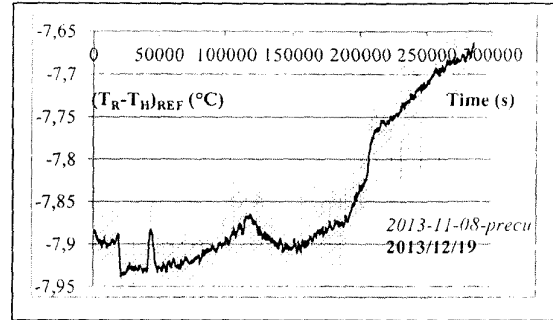


Figure 2' Evolution with time of $(T_R - T_H)_{REF}$

The temperature differences were first corrected for the drift with time (linear correction). **Figures 3 and 3'** below show the drift corrected Temperature differences

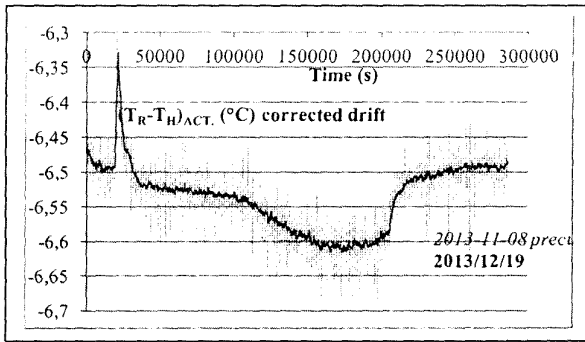


Figure 3 Drift corrected $(T_R - T_H)_{ACT}$

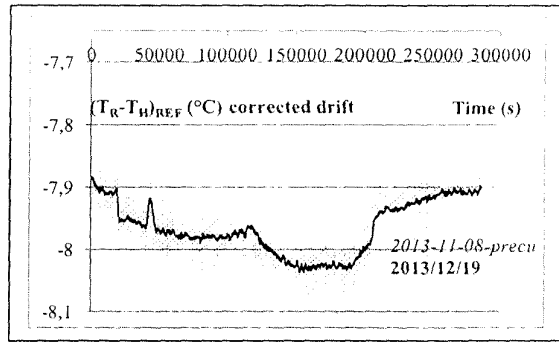


Figure 3' Drift corrected $(T_R - T_H)_{REF}$

The drift corrected temperature differences are then normalized. There is a simple experimental relation between these two differences when the system is under vacuum (no reaction occurs). That is shown in the **Figure 4** below. A polynomial degree 2 is used to normalize $(T_R - T_H)_{ACT}$ versus $(T_R - T_H)_{REF}$.

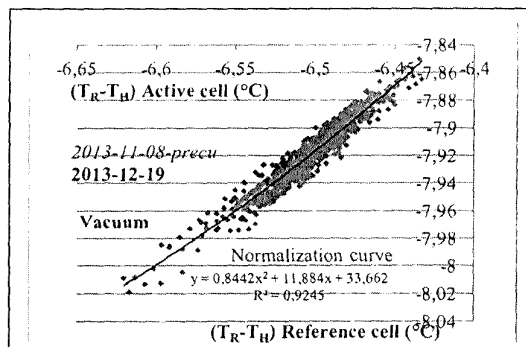


Figure 4 Normalization curve of the temperature differences

The thermal effect in the active cell is then measured by

$$\Delta T (^\circ\text{C}) = ((T_R - T_H)_{ACT})_{\text{norm}} - (T_R - T_H)_{REF} \quad (4)$$

The temperature differences used in relation (4) are the drift corrected ones. **Figure 5** below shows the evolution with time of ΔT , in blue under a vacuum of 4.5 Pa and in red under 8 bar Hydrogen (the green curve is an image of the cabinet temperature variations). The apparent decrease of the energy production at 115,000 s, is probably not due to the temperature decrease of T_{air} , but more likely to a second order differential temperature drift that can be seen at 115,000

s on *Figures 3 and 3'*. No attempt was made to correct this second order alteration. The apparent negative peak at $t=40,000$ s is the result of the calibration run at $t=40,000$ s. This does not modify the energy production in the active cell, but the measured ΔT is reduced to 0.

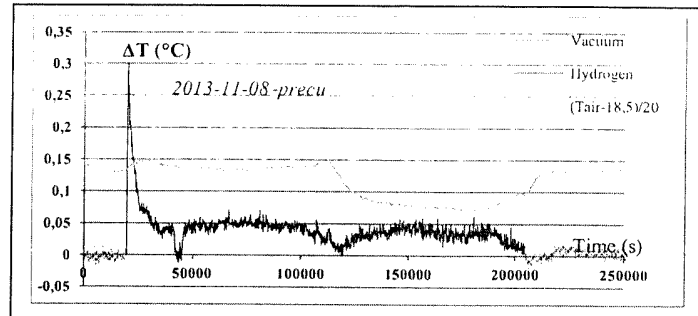
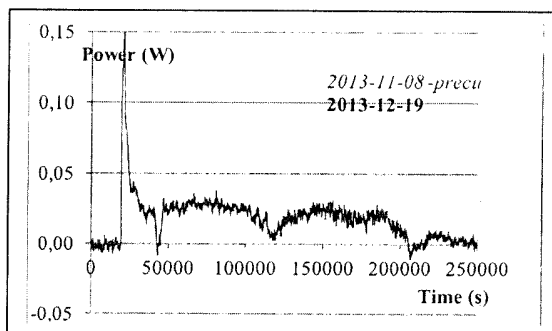


Figure 5 ΔT Evolution with time

The experimental value of a ΔT of $0,04$ °C for an injected power of 25 mW , yields $K=0.62$ W/°C. The differential equation (3) of the calorimeter can be written:

$$dWdt = (MC) \cdot (dT_R)_{ACT} + K \cdot [\Delta T] dt \quad (3')$$

Figures 6 and 7 below show the evolution with time of the power (3') and of the energy produced (integer of (3')).



Figures 6 Power with time

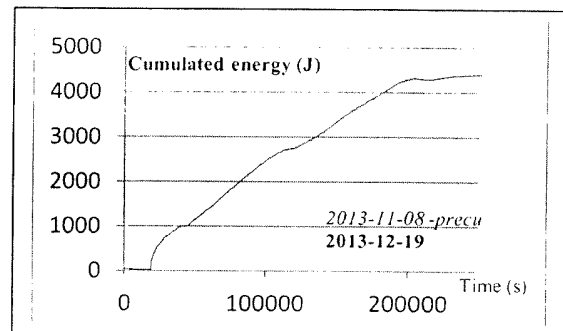


Figure 7 Energy production with time

The value returned by (3') for the calibration is slightly lower than 25 mW ($K = MC/\tau = 0.57$ W/°C-cells dissymetry).

4.2. NiO reduction (experiment 2013-12-15) and run at 550°C (experiment 2013-12-26)

Figures 8 and 9 show the evolution with time of the ΔT 's. The calibration energy at 210000 s (in 2013-12-26) was too high for the real energy production (which can be estimated to be 5 mW, in line with (3') and its integer).

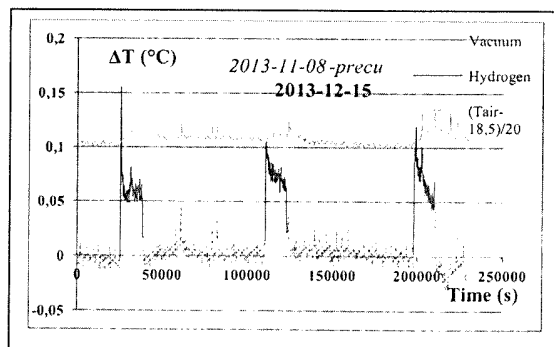


Figure 8 ΔT evolution for NiO reduction

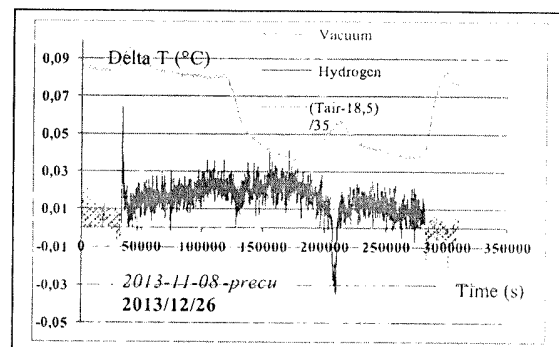


Figure 9 ΔT evolution at 550°C

5. Energy released during the whole experiment

Table 3 below gives the total energy produced during the experiment

Table 3. Total energy produced during the experiment (J)

NiO reduction	1,230
Run at 455°C	4,300
Run at 550°C	2,100
Calibrations	108
Total	7,738

The figure indicated for the calibrations are the calibrations energies that offset the energy production but do not suppress it. The measured energy irreversibly released during the experiment is thus 429.6 KJ/mole Ni.

The Ellingham diagram of the system NiO/H₂ shows that Nickel oxide reduction by Hydrogen is exothermic (25 KJ/mole Ni) under the conditions used.

The net energy irreversibly released in the whole experiment is thus 404.6 KJ/mole Ni. Prior to the experiment a sample of the same powder was run during 180,000 s at 455°C under a vacuum of 4.5 Pa. The measured ΔT was 0 \pm 0.01 °C. With $K=0.6$ W/°C, the lower and upper limits for the energy released are thus 243 and 572 KJ/mole Ni. There is no thermal signature of an endothermic reaction when the system is back to vacuum at the end of an experiment. By contrast the hydrogenation of Titanium powder in the device used, showed a reversible reaction at 455°C (8 bar hydrogen and then a 4.5 Pa vacuum).

No radiations (α , β or γ) were detected above background from the processed powder.

6. Conclusion

The reaction mechanism presented in [2] allows the penetration, inside the Nickel atom, of a polarized dipole formed by an electron coming from the low work function substance (LaB6) and 2 positive charges (the nickel nucleus and a proton adsorbed on the Nickel surface). The reaction product was proposed to be called a Nickel pico-hydride, which is described in Figure 10 below (only the modified K shell of the modified Nickel atom is represented).

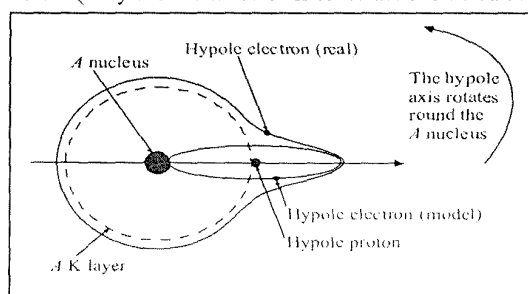


Figure 10 Representation of a Nickel pico-hydride

The pico-hydride is thus described as a 5 particles compound (the nucleus of the atom A and its 2 K electrons, and a couple proton/electron, the hypole H_A). Its stability is achieved by the dissymmetry of the 2 positives charges inducing a dipolar attraction between them. The localization of the oscillating electron of the hypole is constrained by the K electrons of the atom A . The axis A nucleus/hypole proton rotates round A .

Should the formation of this pico-hydride be the explanation of the thermal effect observed in this study, the conversion would have been very low (between 300 and 700 ppm).

Increasing the conversion, evidencing the 8 keV X-Rays emitted during the synthesis of the Nickel pico-hydride and identifying the Nickel pico-hydride isotopes are the objectives of the future work.

References

- [1] C.H. Bartholomew "Hydrogen adsorption on supported Cobalt, Iron and Nickel *Catalysis letters* 7 (1990) 27-52
- [2] J.J Dufour, X.J.C Dufour and J.D Vinko "Pico-chemistry: the possibility of new phases in some hydrogen/metal systems" *International Journal of Modern Physics B* Vol.27, N° 15 (2013) 1362038 (8 pages).

