Programme Committee Proposal Number : ***SI 715***

FIRST X-RAY MEASUREMENTS OF PD_8NI_{92}(110) SURFACE DURING THE BUTADIENE HYDROGENATION REACTION

LIGNE : **ID03** **UHV/HP Chamber**

NUMBER OF RUNS USED : 24

STARTING DATE : 3rd December 2001

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EXPERIMENTAL REPORT

We have performed the first X-ray measurements during the hydrogenation reaction of butadiene (hydrocarbon C4H6), by using the UHV/HP chamber of ID03. This surface is strongly Pd enriched (80%) and exhibits a (Nx1) reconstruction. We took a great care in the preparation of the experiment by a long bake out of the chamber since we had previously observed that the hydrogenation reaction could be inhibited by residual contaminant (especially CO) of other experiments earlier made in the same environment.

First, we did UHV surface preparation and X-ray data collection to determine the structure which generates the (Nx1) reconstruction. The intensity of the superstructure peaks and the value of N were found very sensitive to the residual molecules in the vacuum. Surprisingly, when improving the vacuum, the superstructure intensities were lower and N shifted from 5 to 6. The origin of this reconstruction remains an open question to which a future data analysis should help to answer. We point out that the X-ray patterns for this surface alloy is very different from the one observed for 3-4 ML Pd on Ni(110). In the deposit, we have shown that the (Nx2) is generated by a rearrangement of Pd atoms on the whole surface film.

The system solid/gas was then followed during the hydrogenation reaction with a total pressure of the reactive mixture of 5 mbar and with an initial hydrogen/butadiene ratio of 10:1.

- the evolution of the reactants/products was monitored by a mass spectrometer to analyze the gas in the UHV-HP chamber;
- diffracted intensities were recorded at (0 -1 0.028) on a fundamental rod and at (0 –1/6 0.028) on the superstructure peak.

The main results are summarized on figures.

The two phases of the selective reaction were observed :

1/ During the hydrogenation of butadiene (C4H6 => M=54) into butenes (C4H8 => M=56), the diffracted intensity at (0 –1 0.028) decreases. This phase was twenty minutes long, a duration very similar what was previously measured in a catalysis reactor.

2/ In the second phase, during the hydrogenation of butenes into butane(C4H10 => M=58), the diffracted intensity at (0 –1 0.028) increases.

This process is mainly reversible. After pumping down UHV, the x-ray diffracted intensity recovers the initial value, and after refilling the X-ray chamber the same process develops again.

Conversely and unexpectedly, no correlation has been found between the superstructure peak intensity and the reaction process.

The same experiment was tried just after an Ar^+ bombarding of the surface alloy, but without the subsequent annealing which smoothes out the surface and raises the Pd segregation. No hydrogenation reaction was detected during a time scale of 1 hour. This proves that the observed reaction was not a

Figure 1 : Experience ESRF - 7/12/2001
Hydrogenation du butadiene-1,3 sur Pd_8Ni_{92} (110)

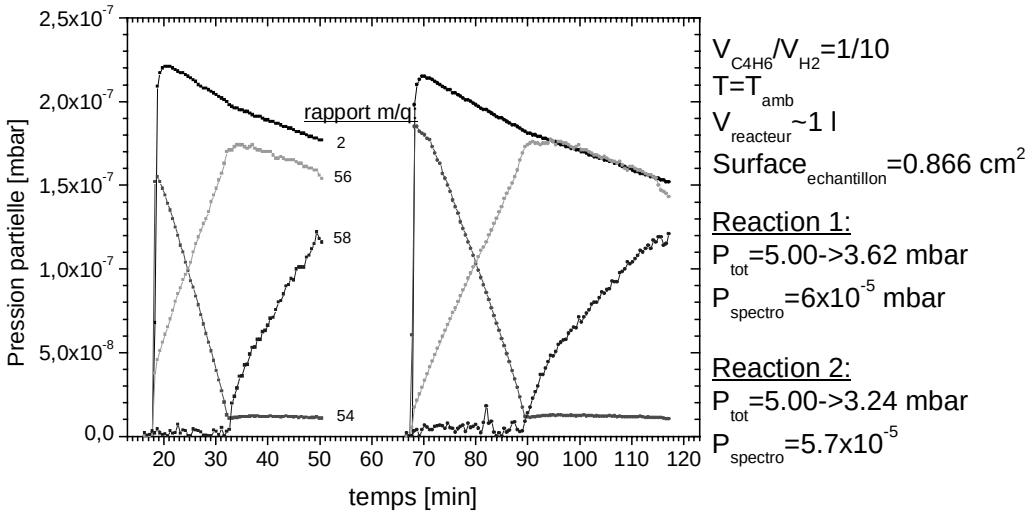
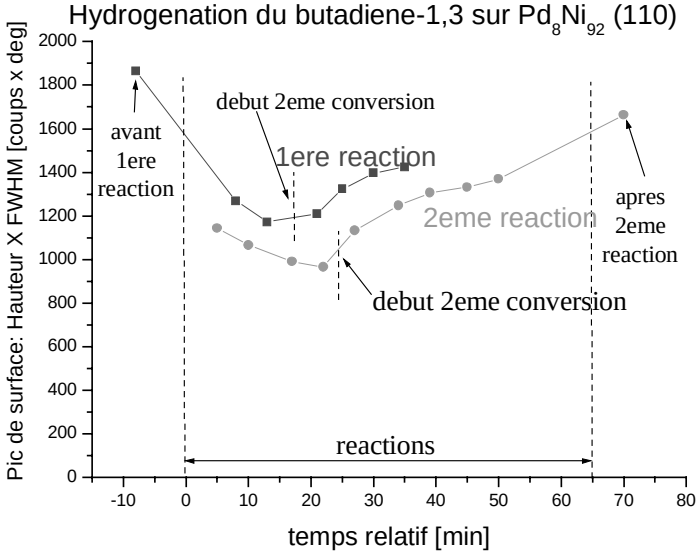


Figure 2 : Experience ESRF - 7/12/2001
Hydrogenation du butadiene-1,3 sur Pd_8Ni_{92} (110)



spurious effect of one of the components in the chamber and only correlated to the strained Pd at the annealed surface alloy.

We also studied the effect of hydrogen for the same pressure (5 mbar) : we observed at the same reciprocal lattice point (0 –1 0.028) as in figure 2, a rapid intensity decrease of about 15%, and then a stabilization to a constant value during the whole exposition times. After pumping down to UHV the diffracted intensity goes back to the initial intensity.

As a preliminary conclusion of this experiment, we have, for the first time evidenced real time changes in the surface structure of Pd8ni92 by x-ray diffraction *in-situ* measurements during the hydrogenation reaction.

This shows the feasibility of such experiments, but in order to conclude on the precise structural changes in each step of the reaction, a set of in-plane data and scans along rods must be recorded allowing complete structural analysis.