



ESRF

Experiment title:

IN SITU EXAFS OF MODIFIED RHODIUM
SUPPORTED CATALYSTS

Experiment number:

CH-163

Beamline: Date of Experiment:

GILDA-CRG D8

from: 21 FEBRUARY

to: 26 FEBRUARY 1996

Date of Report:

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Shifts: Local contact(s):

15

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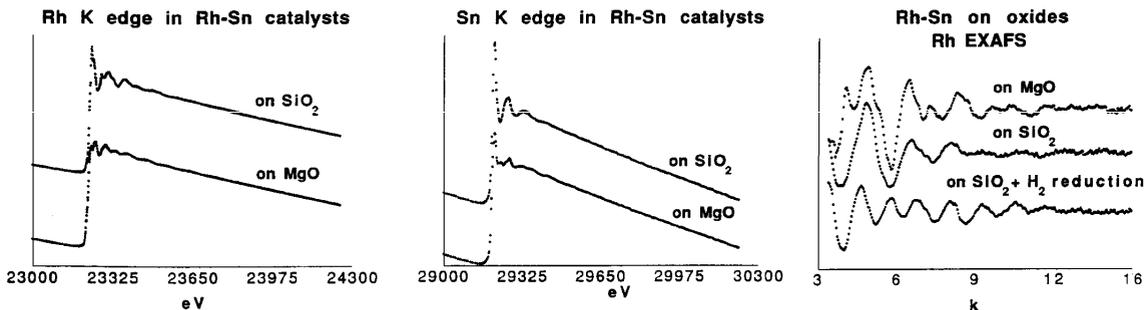
Report:

In the following we report on the results of our last run. We already described, in the previous Experimental Report, the relevant results from our previous activity at ESRF on the same beam line, based on the shifts assigned by ESRF Review Committee to our project CH-34, On Pd supported catalysts. These results have been part of a graduation thesis ("laurea" in Chemistry) and are now being **collected in a forthcoming paper.**

We made use of the shifts assigned to project CH-163 to investigate, by in situ EXAFS in transmission mode, bimetallic rhodium-based catalysts indifferent supports. We obtained quite satisfactory results, as reported hereafter, yet we were not able to complete our data collection because of a beam time loss of some **18 hrs**, due to troubles with the RF and the injection system (22 and 23/2). We made use of our furnace for gas treatments, which now allows for mounting (in a dry-box) and controlled transferring of air-sensitive samples, heating up to 500°C (without water cooling) and **gas treatments.** Some work is still due to set-up the already existent liquid N₂ cooling system, because of geometric constraints of the experimental Gilda chamber.

In order to fully characterize the bimetallic system by means of measurements at the two relevant metal edges, we concentrated on Rh-Sn supported catalysts. Switching from Rh (23000 eV) to Sn (29000) K edges typically required 10 min. This allowed us to complete 4 reduction treatments on impregnated and/or calcined samples.

We always collected data at least 3 times per sample per edge, in order to be able to statistically analyze the data. The systems investigated were a series of Rh-Sn catalysts on MgO and SiO₂ prepared from chloride precursors at low metal content (2-4 wt%) and a series of selected reference compounds, pure oxides and supported species. The interest in the Rh-Sn systems is mainly related to the enormous difference in the catalytic activity for hydrogenation, shown by Rh-Sn, in particular proportions, on the two supports, which calls for a specific role of the substrates. We are interested in determining differences in the coordination environment, in an effort to elucidate the interplay smog structural and electronic effects. Evidences for these last effects were obtained by means of catalytic and conventional (ir, TYPD, TPRD, etc.) measurements. Due to the schedule of our runs, data elaboration is at the very beginning. However, some relevant results are already at hand: large differences between the silica and magnesia-supported species were found in the case of the catalyst precursor, obtained by calcination of the impregnated solutions. This holds for Rh and for Sn, as can be clearly seen in fig.1 for the absorption spectrum at Rh K-edge, in fig.2 for the corresponding Sn K-edge and, more clearly, from the EXAFS signals of Rh, shown in Fig. 3.



The structural differences are apparent also after the activation step (reduction in H₂ at 450 °C) and could be related to the formation and growth of particles with different average size. There is a clear correspondence of our findings with the catalytic activity, which abruptly drops from MgO to SiO₂-supported bimetallic Rh-Sn species. Our hypothesis of a different nucleation of the particles after activation is now strengthened. Further data analysis work is expected to lead to a more detailed comprehension of the very distinct catalytic behaviour.

Finally, we want to thank the Gilda team for enthusiastic and competent support all through our experiments and the personnel at ESRF for their help in all the aspects of their competence.