



**Experiment title:**  
STRUCTURAL CHARACTERIZATION BY IN SITU EXAFS  
OF SILICA GRAFTED TRIPHOSPHATE Rh(1) CATALYSTS

**Experiment  
number:**  
CH-220

**Beamline:**  
GILDA-BM8

**Date of experiment:**  
from: 15-11-96 to: 18-11-96

**Date of report:**  
28-2-97

**shifts:**  
9

**Local contact(s):**  
Francesco D'Acapito

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**Names and affiliations of applicants** (\* indicates experimentalists):

L. Sordelli*,	CNR c/o University "Statale" of Milano, ITALY
G. Vlaic,	University of Trieste, ITALY
J. Evans,	University of Southampton, UK
R. Zanoni,	University "La Sapienza" of Roma, ITALY

**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-163, on promoted Rh supported catalysts. These results have been part of a graduation thesis and a paper based on them has just been submitted to the Applied Catalysis.

We made use of the nine shifts assigned to project CH-220 to investigate, by in situ EXAFS in transmission mode (Si(311) double crystal monochromator), rhodium catalysts obtained by anchoring the organo-complexes [(sulphos)Rh(cod)] and [(sulphos)Rh(CO)<sub>2</sub>] on the silica surface with a metal loading of 1.5wt.%. The samples have been treated and measured inside our furnace-cell which allows for loading (in a dry-box) and transferring of air-sensitive samples, heating up to 500°C, quick air cooling and gas treatments. Some work is still due to set-up the already existent liquid N<sub>2</sub> cooling system, because of geometric constraints of the experimental Gilda chamber.

Spectra were collected at the Rh K-edge, with the coaddition of 3 complete scans per sample, in order to perform a statistical analysis of the data. Due to a temporary breakdown of the monochromator flat crystal, dynamical focusing was not possible, with a cosequent highly variable beam spot dimension during the scans. Still exafs spectra were of satisfactory quality up to 13Å<sup>-1</sup>, where the edge jumps were of about 0.2 a.u.

In order to better resolve the cumbersome structure of the [(sulphos)Rh(cod)] and [(sulphos)Rh(CO)<sub>2</sub>] complex exafs signal, to which a many shells scattering contributes, many reference Rh compounds of known crystallographic structure, which have either phenyl-phosphine or cod/CO ligands, have also been analysed.

Due to the the necessity of multiple scattering analysis, data fits elaboration is still in progress. However, some relevant results obtained by comparison among the fourier-transformed data are already at hand:

after the impregnation onto the silica the [(sulphos)Rh(cod)] complex is deposited intact on the surface; this strongly suggest that the grafting occurs through the sulphonated tail, probably with the hydroxil surface groups (in agreement with the higher precursor loading observed when the silica is outgassed at lower temperatures). The reduction in hydrogen removes the cod ligand without originating formation of contiguous Rh-Rh sites but inducing the lengthen of one of the Rh-P distance (as shown in Fig. 1 by the FT spectra comparison). This fact supports the hypotesis that in heterogeneous phase isolate sites of Rh(1) are not active for the hydroformylation reaction. Probably, due to the highly reduced mobility on the support surface, the reversible opening of a phosphin arm, mechanism accounted for the hydroformylation activity of this complex in the homogeneous phase, is prevented. The carbonylation at room temperature of the reduced sample originates spectra whose initial analysis suggests the presence of only one carbonyl ligand, while after prolonged contact with the  $\text{CO:H}_2$  mixture at  $120^\circ\text{C}$  (reaction temperature), the spectra very much resemble those of the just impregnated [(sulphos)Rh(CO) $_2$ ]/SiO $_2$ . In Fig. 2 the comparison is shown among the FT spectra of the pure cabonyl complex, the silica supported carbonyl complex and the supported cod complex after reductive cod elimination and re-carbonylation at room temperature. Successive exposure to  $\text{N}_2$  and  $\text{O}_2$  at temperatures up to  $150^\circ\text{C}$  demonstrated the high thermal stability of the supported carbonyl complex, in agreement with the FT-IR data and with the hypothesis that the preferential coordination of CO on Rh sites acts as a poison in the hydroformylation reaction.

Fig. 1

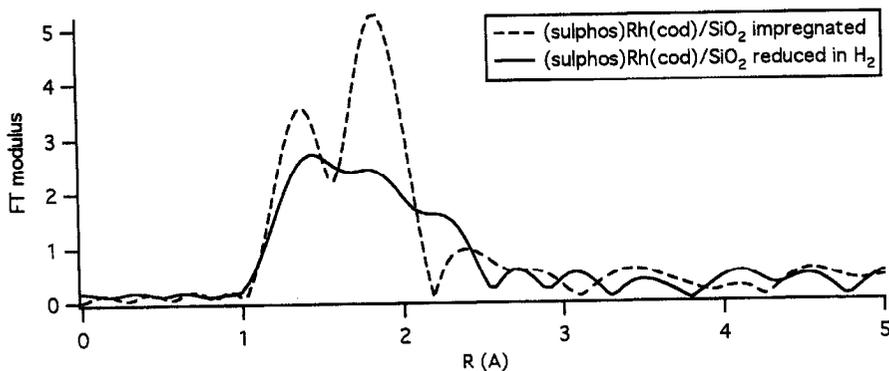
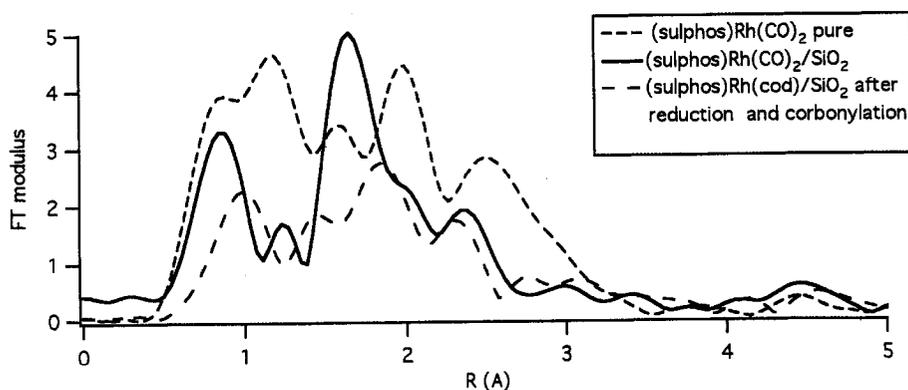


Fig. 2



We thank the Gilda team for the competent support all through our experiments and the personnel at ESRF, especially the Chemistry Laboratory responsible, for their help in all the aspects of their competence.