

**Experiment title:**

IN SITU EXAFS OF PROMOTED Pt/MgO CATALYSTS IN THE UNSATURATED ALDEHYDES SELECTIVE HYDROGENATION REACTION

**Experiment****number:**

CH-465

**Beamline:**

GILDA-BM8

**Date of experiment:**

from: 28-1-98 to: 5-2-98

**Date of report:**

28-2-00

**Shifts:**

18

**Local contact(s):**

Francesco D'Acapito

*Received at ESRF:***- 2 MAR.2000****Names and affiliations of applicants (\* indicates experimentalists):**

L. Sordelli\*, CNR c/o Dip. Chimica Inorganica, University of Milano, ITALY  
G. Vlaic, Dip. Scienze Chimiche, University of Trieste, ITALY  
E. Fonda\*, Dip. Scienze Chimiche, University of Trieste, ITALY  
P. Colavita\*, Dip. Scienze Chimiche, University of Trieste, ITALY  
D. Andreatta\*, Dip. Scienze Chimiche, University of Trieste, ITALY

**Report:**

We made use of the 18 shifts assigned to project CH-465 in the period 28 January-5 February 1998 to investigate, by in situ EXAFS, Pt-Sn catalysts obtained by anchoring the organo-complexes Pt(acac)<sub>2</sub> and Sn(But)<sub>4</sub> on the magnesia surface with a Pt metal loading of 1-2 wt.%. 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. All spectra were recorded at 300 K in transmission mode at the Pt L<sub>III</sub> and Sn K edge over the range 11.5-12.5 keV and 29-30.2 keV, using the Si[311] and Si[511] double-crystal monochromator respectively, with a sampling step of 2 eV and an integration time of 2 s for each point. Incident and transmitted photon fluxes have been detected with ionisation chambers filled, respectively, with 0.1 and 0.4 bar of Kr. Each spectrum has been acquired three times. The powder samples were loaded under inert atmosphere, reduced in-situ in H<sub>2</sub> flow at 623 K in a catalysis-EXAFS cell (Lytle type), and cooled down to room temperature before spectra acquisition. Sample homogeneity was checked by reading the transmitted photo-current while scanning the sample area along the x-y axes.

Due to the necessity of interchanging the monochromator crystal when moving from 11564 eV to 29200 eV, all samples have been first measured in-situ at the Pt L<sub>III</sub> edge at the end of each treatment step, and then at the Sn K edge after repeating the in-situ treatments. Problems occurred during the beam-line set-up for the high energy configuration and with the electronic of the data acquisition system, resulted in the loss of most of the beam-time, that was then rescheduled in the period 13-17 June 1998.

Extracted  $\chi(k)$  data have been averaged before the EXAFS data analysis. Standard deviation calculated from the averaged spectra ( $1-4 \cdot 10^{-3}$ ) was used as an estimate of the statistical noise for the evaluation of the errors associated with each structural parameter. Experimental  $\chi(k)$  data were extracted from absorption data by a conventional procedure (pre-edge region linear background, polynomial fitting for the atomic-like contribution, Lengeler and Eisenberger normalization procedure). The  $k^3$ -weighted  $\chi(k)$  data were Fourier transformed over a typical  $k$  range of 3-15  $\text{\AA}^{-1}$ . Main contributions to the Fourier transform modulus were filtered in order to obtain metal nearest-neighbour shells. The so obtained filtered contributions were analysed using the programs developed by Michalowicz. Phase shift and amplitude functions of scattering atoms have been extracted from the experimental spectra of the following systems: Pt foil, Sn foil, Pt(acac)<sub>2</sub>, SnO<sub>2</sub> and Pt<sub>6</sub>-Sn<sub>6</sub>, anion cluster complexe of known structure.

The study was aimed to the investigation of the relationships between structure and catalytic performances of a series of Pt-Sn/MgO systems, which have shown a strong dependance on the preparation methodology, the system Pt<sub>IMP</sub>-Sn<sub>CVD</sub>/MgO [IMP= impregnated from Pt(acac)<sub>2</sub>; CVD= vapor deposition from Sn(Bu)<sub>4</sub>, Sn/Pt molar ratio =0.5] being the most active and selective system. When activated in reductive mixture (H<sub>2</sub>:He=0.06 flow at T=500°C) it has a 80% selectivity versus the 15% selectivity in absence of Sn [1]. In this case FTIR spectra suggest the presence of a "cherry" bimetallic structure with the Pt in the core. It's notable that the same catalyst after reduction in pure H<sub>2</sub> flow at 500°C gives a less active system, while higher Sn/Pt ratios produce completely not active catalysts. In every case the Pt-Sn/MgO catalysts need an induction period prior being very selective toward unsaturated alcohols. During this period the C=C is predominately hydrogenated. This behaviour can be explained by hypotizing a surface reconstruction process. The great deal of catalytic results, together with IR, TPD and TPR characterization, needed to be supported by a local structure determination of the active metal sites under close-to-real catalytic conditions and during activation treatments. In particular, the occurrence of surface enrichment in one of the two metals, and the morphological reconstruction of the catalytically active phase prior and after the induction period previously mentioned were observed. Moreover, due to the impossibility in obtaining reliable dispersion data from hydrogen chemisorption measurement when the metal is supported on MgO, EXAFS data also provided fundamental information on the supported particles mean diameters and dispersion degree.

The importance of working at both metal edges in order to determine the role and location of the catalyst promoter has been confirmed: the difference between the Pt and Sn scattering amplitude functions made possible a clear discrimination of the two metals as scatterers and provided relevant informations on the bimetallic phase structure and morphology at different Pt loading and Sn/Pt molar ratios.

The data collected during this experiment have produced a thesis work and a paper in progress to be submitted to the Applied Catalysis.

[1] Dossi C., Recchia S., Fusi A., Sordelli L., Psaro R., *15th Meeting of the North American Catalysis Society*, Chicago, May 18-22, 1997, Poster Program, P 137.

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