

Gas sensitive Pt containing organometallic macromolecules: metal - gas interaction studied by EXAFS

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Introduction

The main objective of this project was to establish a relationship between chemical, geometrical and electronic structure of small Pt containing organometallic systems (no more than four repetitive units) and their sensitivity and selectivity with regard to the sulphur containing molecules SO₂ and H₂S. Poly-ynes consisting of Pt or Pd square planar complexes in the chain between organic spacers have been synthesized and characterized in our group [1]. Our systems have been successfully used in sensors and optical devices[2]. Structural data have been achieved on these materials by means of SR-XPS, NEXAFS [3], reflEXAFS and EXAFS [4]. The simpler related model molecules, recently synthesized to have model systems whose characterization would be crucial for the interpretation of the polymers chemical physical properties, have been studied by XPS and EXAFS and a square planar structure around the metal and a charge transfer interaction between units [5] were assessed.

Experiment

EXAFS spectroscopy was performed at the Pt L_{III} edge to investigate the interaction between Pt-DEBP_n (Pt-diethynylbiphenyl, n = 2,4) oligomers of different length and geometry (linear and cyclic, depending on the Pt square planar complex configuration, *trans* or *cis* respectively) and SO₂, H₂S molecules. The hypothesized chemical interaction occurring between Pt(II) and S was verified and investigated. We believe that this chemical interaction is responsible for the high sensitivity and selectivity of Pt-DEBP_n based mass sensor devices towards sulfur-containing compounds [2].

As a start, we performed EXAFS measurements on the sample pellet in low vacuum conditions (P = 10⁻³ mBar). Then, we filled up the GILDA's chemical cell with SO₂ at a partial pressure of about 500 mBar, then we performed the same structural characterization. *In situ* treatments were made possible at GILDA by a small chamber equipped with input and output gas lines, that allows to perform EXAFS measurements on samples in controlled chemical environment [6]. We made the same procedure with H₂S.

The experiments were carried out by EXAFS measurements on Pt-DEBP_n pellet samples, both in low vacuum conditions (P = 10⁻³ mBar) and in presence of SO₂ or H₂S gas (P = 500 mBar). Detection of the transmission signal was done at the Pt L_{III}-edge (11564 eV).

Results

EXAFS measurements gave evidence for the interaction between the metal, covalently bonded to the diethynyl-macromolecule, and the H₂S gaseous molecules; structural modifications at the Pt coordination centre have been detected as a consequence of this interaction. SO₂ molecules seems not to interact with our samples, thus confirming the selectivity of Pt-DEBP_n as sensors.

Data analysis is currently in progress; at this stage, we can confirm that Pt-DEBP_n samples interact with H₂S molecules showing a S-Pt coordination. Preliminary data analysis shows that the structural order of the first neighbours surrounding the absorbing metal is different in vacuum and in H₂S environment. More in detail, in the pristine sample a square planar structure around the metal was assessed [4,5], while after H₂S exposure data analysis suggests that the Pt center is more likely to be pentacoordinated.

No interaction between Pt and S has been evidenced for samples exposed to SO₂. The selectivity of our materials as sulfur-containing molecules sensors has been verified.

References

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