



	Experiment title: HYBRIPUR PROJECT: CHARACTERIZATION OF NEW ORGANIC-INORGANIC HYBRID POLYMERS FOR CATALYTIC APPLICATIONS	Experiment number: CH-718
Beamline: ID12-A	Date of experiment: from: November 24th to: November 29th, 1999	Date of report: 1rst March 2001
Shifts: 18	Local contact(s): J. GOULON and A. ROGALEV	<i>Received at ESRF:</i>

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Report:

The goal of the HYBRIPUR project is to develop and characterize new *organic-inorganic hybrid polymeric materials* for catalytic applications concerned with the purification or activation of gases. These materials are prepared by *Sol-Gel* processes involving the co-polycondensation of macrocyclic complexes substituted with trialkoxysilyl terminal groups: $-\text{Si}(\text{OR})_3$ [1]. The macrocyclic ligands are essentially tetraza-, tetrathia- cyclams or cyclenes (and porphyrins). With the immobilisation of the macrocyclic ligand in an inorganic polymeric network, it is possible to tailor catalysts with optimized efficiency, long life-time and easy regeneration. The partners associated in this project are: the CNRS, AIR-LIQUIDE, RHONE-POULENC and the French Ministry for Research and Advanced Technologies. The ESRF proposal CH-718 focused on the structural characterization using EXAFS and XANES of a specific class of Cu catalysts which can complex molecular oxygen in a reversible way and with an excellent efficiency. This proposal ranked #1 on the reserve list of beamline ID12A was finally allocated beamtime.

Using the undulator micro-gapscan technique, EXAFS spectra of high quality were recorded at $T=80\text{K}$ in the fluorescence mode at the Cu K-edge for a variety of xerogels which were known to exhibit fairly different catalytic efficiencies: active GD856/CuCl₂ under N₂ or O₂; weakly active GD855/CuBr₂ under N₂ or O₂; inactive GD285:CuCl₂ under O₂ ... For the sake of reference, EXAFS spectra were also recorded under the same conditions for a few model compounds including the copper porphyrin TPP:Cu and various substituted cyclams such as TMC:Cu, 2BF₄ and less common species like GD644P. Since the EXAFS oscillations could be extracted systematically up to $k_{\text{max}} = 21 \text{ \AA}^{-1}$, the corresponding FT spectra had a very good resolution which allowed us to identify unambiguously not only the signals of the coordinating Nitrogen atoms but also of the more disordered Carbons of the macrocyclic backbone [2]. Using *Difference Analyses* [3], we established that the active center was a “skew” binuclear arrangement of the Cu atoms in the slightly

distorted square planar ligand field of the 4 Nitrogen of the substituted cyclam. The Cu...Cu distance was found to be $5.05 \pm 0.05 \text{ \AA}$; oxygen is bridging the Cu atoms with a typical Cu...O bond length of $2.14 \pm 0.01 \text{ \AA}$ and an estimated Cu-O-O angle slightly in excess of 120° . In the case of the weakly active precursor GD856/CuCl₂ under N₂, we failed to give any definitive proof of the (probable) coordination of a labile (disordered) Cl atom, whereas the presence of a tightly bound axial Cl atom was unambiguously established in the case of the inactive xerogel GD285:CuCl₂. EXAFS spectra recorded at the Cl K-edge did not bring any additional information and were spoiled by the undesirable absorption edge of residual K⁺ cations. Interestingly, however, we found that in the case of the poorly active xerogels GD855/CuBr₂ under N₂ or O₂, one axial bromine atom was also tightly bound to the Cu site.

High quality XANES spectra were also recorded which allowed us to extract narrow shape resonances after numerical deconvolution accounting for the instrumental + core hole life-time broadening. These spectra were then systematically compared with *ab initio* simulations performed with the advanced MSW code "FDMNES" in which charge transfer effects can be taken into account with various degrees of sophistication. Starting with a series of model compounds of known crystal structure(e.g. TPP:Cu and cyclams) we found possible to generate *ab initio* XANES spectra in remarkable agreement with the *deconvoluted* experimental spectra. We confirmed that there is a quite significant charge transfer from the Nitrogen atoms towards the central metal and that not only the partially filled 3d band but also the 4p orbitals are essential in this process: in nearly all our systems we were able to identify a well resolved (strong) resonance involving the 4p orbitals of the metal together with the 2s2p orbitals of the Nitrogen ligands. Note that this resonance is remarkably enhanced in the case of the active catalysts. Further simulations still underway suggest that, as a consequence of the strong charge transfer from the Nitrogen atoms towards the metal, the active site may behave as mixed valence Cu(I) – Cu(II) species while the "formal" chemical valency should be 2+. Our interpretation would be consistent with the very weak EPR spectra recorded on the active xerogels and with the established fact that only Cu(I) is known to bind molecular oxygen.

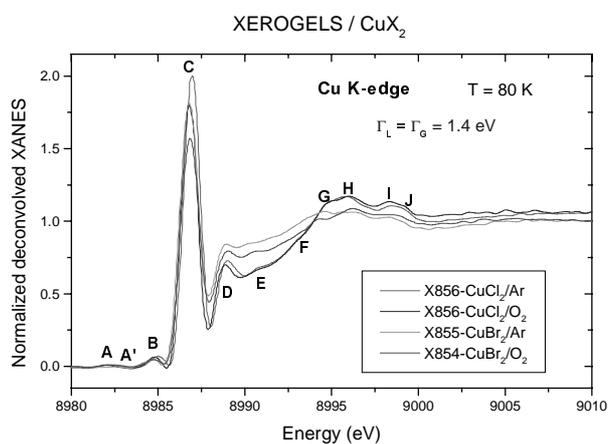


Fig. 1 Deconvoluted Experimental XANES spectra of xerogels complexed with CuCl₂ and CuBr₂

Note the intense resonance $1s \rightarrow 4p$ that is sensitive to the ligand field and charge transfer

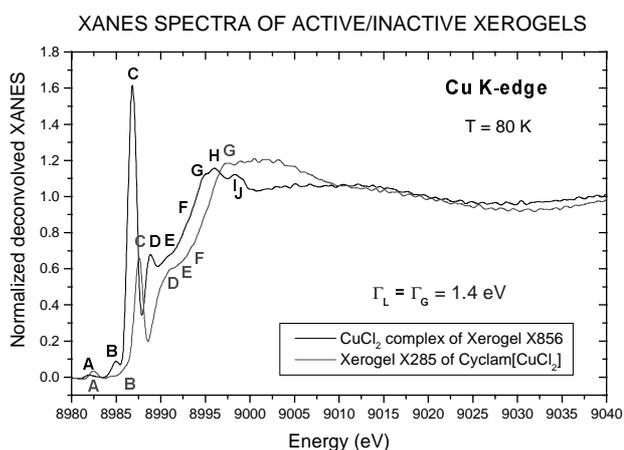


Fig. 2 Deconvoluted Experimental XANES spectra of the catalytically active / inactive xerogels

References:

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