

ESRF-report

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Title : ***Copper complexes as probe for surface molecular patterning in mesostructured silica.***

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Introduction

All the experiments have been performed at the copper K edge with a Si(220) monochromator as planned. Our machine time scheduled in march has been delayed late in the summer (31 of august, 1,2 and 3 of October). This explains a late and only preliminary analysis of our data. Furthermore, it was a first contact of our laboratory with ESRF. Only one of us (LB) had previous experience on other synchrotron facilities in XAFS studies. Two PhD students have been initiated to XAFS on BM30B, S. Abry and S. Calmettes, which should be a key technique for their thesis work. In addition, this first contact on this particular line has been very precious to realize all constraints that should be taken into account to design an *in situ* and low temperature measurements cell in both transmission and fluorescence mode.

Experimental goal

Our study concerned copper at the oxidation state 2 and used as a probe for adsorption sites on nanostructured silica of high surface area (900 m²/g). The originality of our study relies on the partial hydrophobization of the silica internal surface according to a new method developed in our laboratory and called molecular stencil patterning. This method is designed to create hydrophilic nano-island isolated one to another where adsorption may operate. Tetraamminecopper (II) is adsorbed at 25°C. The absence of the nitrate counterion in the silica is consistent with a strong adsorption as hydroxide precipitate, surface silicate or isolated adsorbed complexes. The isolated adsorption site would be characterized by the absence of Cu-O-Cu correlations as expected in hydroxides or silicates and by the formation of one or two Cu-O-Si bridges, only. Ideally, it would be a neutral diamminedisilanolatocopper(II) surface complex, [Cu(NH₃)₂(SiO)₂]. The site isolation do not occur on a genuine silica surface leading to surface copper silicate with a mixture of copper and silicon in the second coordination shell but should operate on a modified silica as such as ours. However, chemical analyses reveal a nitrogen to copper smaller than 2 and EPR signals that were difficult to interpret. The second shell analysis of the EXAFS signal should help us to solve the problem.

XAFS measurements

12 samples and four references were investigated for this study during the first three days. In this first series. The samples were design with a varying level of hydrophibization to modulate the isolation effect. The measurements were performed at room temperature on pellets of the sample diluted in boronitride, BN and finely grounded in a mortar. The references were chosen to get pure oxygen or oxygen-nitrogen mixture of first copper coordination sphere, CuSO₄.5H₂O for CuO₄(O_{JT})₂, [Cu(en)₂].2NO₃, CuN₄(O_{JT})₂, [Cu(DPA)]₂.2NO₃, CuN₃(O_{JT})₂, where O_{JT} stands for ligand position stretched or squeezed by the Jahn-Teller effect. We need to have a silicate as a reference (diopase or chrysocolla) that will be investigated in the next runs.

All measurements were collected in an energy range large enough for a pre-edge baseline extraction and, in the EXAFS range up to a value of 16 in k space. Detection was taken in fluorescence and transmission modes on the sample and simultaneously on a copper metal foil in transmission mode. Four to seven spectra were taken for each sample depending on the concentration of copper to get a satisfying signal to noise ratio.

We have observe that all EXAFS signals vanish between $k = 13$ to 14 . The preliminary EXAFS analysis clearly shows that a satisfying second coordination shell analysis is possible on the transmission signal for most of the cases and in the all cases on fluorescence signals. A more detailed analysis will allow us to discriminate copper to silicon in the second shell.

The supplementary day of machine time has been devoted to start the study on copper complexes grafted on partially hydrophobized silicas described above. Here, the copper is not adsorbed directly in the hydrophilic “hole”. The organic polyamine ligand is grafted first acting as an anchor between copper and the surface. 6 samples were investigated. The preliminary study reveals that Cu-O-Cu and Cu-O-Si contributions are barely detectable showing that site isolation has operated and that that copper does not “see” the silica surface despite the short length of the anchor (3 carbon chain). A thorough analysis is necessary to definitively conclude on these points.

Conclusion

This first experience of our team on the BM30B line for XAFS measurements has been very positive. Two students are now familiar with the usual operating conditions. The feasibility of our experiment is fully confirmed. A design of an *in situ* cell is now on progress. The preliminary analysis suggest some improvements on the first series of samples. The supplementary day has been used to start another very promising set of samples of copper complexes grafted in our nanostructured and organically modified silicas, our bio-inspired heterogeneous catalysts.