XAS on Rh and Ir metal sites in post synthetically functionalized UiO-67 Zirconium MOFs

L. Braglia[1,2], E. Borfecchia[1], K. A. Lomachenko[1,2], S. Øien[3], K. P. Lillerud[3], C. Lamberti[1,2]

[1]University of Turin, Department of Chemistry, NIS and CrisDi interdepartmental centers and INSTM reference center, Via Pietro Giuria 7, 10125 Turin (Italy)

[2]Southern Federal University, Faculty of Physics, Zorge 5, 344090 Rostov on Don (Russia)

[3]inGAP Centre for Research Based Innovation, Department of Chemistry, University of Oslo, P.O. Box 1033, N-0315 Oslo, Norway

luca.braglia@unito.it

Abstract. We synthesized UiO-67 metal-organic-frameworks (MOFs) functionalized with different transition metals (Rh, Ir). Using EXAFS we verified that the synthesis has been successful. Furthermore, we observed the change of local environment while varying of metal site. XAS spectroscopy is the most informative technique to characterize these kind of materials and to study the local environment around the metal site.

1. Introduction

Metal-organic frameworks (MOFs) are crystalline, porous solids consisting of metal ions or clusters, coordinated with organic molecules. The large number of combinations for inorganic and organic building units offers an infinite variety of structural solutions with a wide range of properties [1]. The recently discovered UiO-66 and UiO-67 classes of iso-structural MOFs are obtained connecting $Zr_6O_4(OH)_4$ inorganic cornerstones with 1,4-benzene-dicarboxylate or 4,4′biphenyl-dicarboxylate linkers, for the UiO-66 and UiO-67 MOFs, respectively [2]. Due to their outstanding stability at high temperatures, high pressures and in presence of different solvents, these materials are among the few MOFs already commercialized for applications in the fields of catalysis, H_2 storage, and gas purification. We are currently exploring the possibility to enhance the capabilities of the UiO-67 MOF by grafting to the framework an additional catalytically-active metal center, by chelating bipyridine-dicarboxylate (bpydc) linkers. The resulting metal-functionalized MOFs are attractive candidates for industrial applications aiming to heterogenization of homogeneous catalytic reactions [1]. In a recent study [3] we have characterized Pt-functionalized UiO-67 using three types of syntheses and followed the reactivity of this system towards molecules of small- (e.g. H_2), medium- (e.g. Br_2), and large-size (e.g. thiol). After these interesting results obtained with Pt, UiO-67 derivatives functionalized with different transition metals were prepared, targeting different kinds of catalytic reactions. Herein we report a preliminary XAS-based study on UiO-67 functionalized with Rh, Ir and Au in *in situ* conditions to demonstrate the effectiveness of synthesis procedure.

2. Experimental and Methods

2.1. Sample preparation

The samples were prepared by post-synthesis functionalization (PSF) approach, where premade UiO-67 MOF was suspended in a solution of precursor metal chloride salts. 4,4'-biphenydicarboxylic acid (H_2bpdc) 2,2'-bipyridine-5,5'-dicarboxylic acid (H_2bpydc) and 2-phenylpyridine-5,4'-dicarboxylic acid (H_2ppydc) were used as linkers in the MOF synthesis; the latter is fundamental for providing the chelating site where the metal functionalization occurs. The employed functionalizing metals were Rh, Ir and Au, using $RhCl_3$, $IrCl_3$ and $HAuCl_4$ as precursors, respectively using the same strategies detailed elsewhere for Pt [3]. Thereby the whole sample set included: UiO-67 bpydc-Rh, UiO-67 bpydc-Ir, UiO-67 ppydc-Ir and UiO-67 ppydc-Au.

2.2. X-ray Absorption Spectroscopy measurements

Due to the local character of the functionalization process, XAS spectroscopy has played a key role in clarifying the local structural and electronic properties of the grafted metal centre [4]. We performed our experiments in Max Lab II (Lund, Sweden) at I811 beamline and in ESRF (Grenoble, France) at BM23 beamline. The white beam in I811 is produced by a liquid He-cooled superconducting wiggler operating with a current around 200mA. We did not use mirrors, and the radiation was selected by a horizontally sagitally focused double-crystal Si(111) monochromator detuned to 20% to minimize the third harmonic. The energy beam was detected by 30 cm ionization chambers for I_0 and I_1 and by photodiode for I_2. We operated in transmission mode above the Ir-L_3 edge (11215 eV) and Au-L_3 edge (11920 eV). The white beam at BM23 was focused in a vertical aperture of 0.3 mm, then the energy beam was selected by a double-crystal monochromator Si(111) and the higher harmonics were suppressed by a Pt-coated mirror at 2 mrad. We collected the data in transmission mode at the Rh-K edge (23220 eV). Three ionizations chambers detected the energy for I_0, I_1 and I_2. An ad hoc cell was used to host the samples [5], in the form of self-supporting pellets of optimized thickness. The XANES and EXAFS spectra were collected in flux of He at room temperature. The data were extracted and analyzed with Athena and Arthemis codes [6].

3. Results and Discussion

The strategy used to fit our data has been to use the amplitude and the Debye Waller factor of chlorine (σ_{Cl}^2) obtained from the fit of reference metal salt samples, while the σ_N^2 values have been estimated on the basis of the analysis previously performed on the Pt-UiO-67 system [3]. The metal in the $RhCl_3$ and $IrCl_3$ reference compounds is assumed to be six-coordinated with six Cl ligands, in octahedral geometry (Table 1). Once the fit of the salt was acceptable, we set its amplitude (S_0^2) in the fits performed on functionalized MOFs. The EXAFS analysis has been performed in the first shell with k^3 weight extraction, the k_{max} was 14 Å^{-1} for all the samples. Figure 1 reports the XANES spectra for UiO-67 functionalized with Rh (a), Ir (b) and Au (c); the MOFs are indicated with orange lines (bpydc linkers) and red lines (ppydc), while the salts are reported as grey lines. XAS has allowed us the ineffective of Au grafting in the UiO-67 ppydc-Au. Indeed, in this case the XANES of the precursor (grey) and after the reaction with the MOF (orange) are exactly overlapped (see Figure 1c).
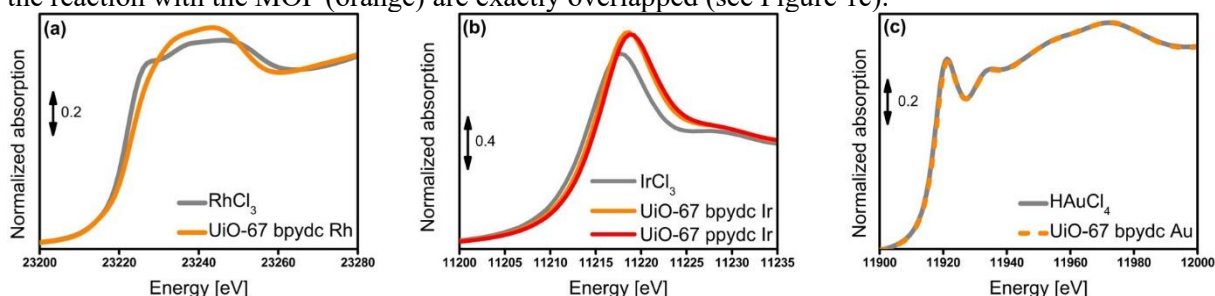

Figure 1. XANES spectra at Rh K-edge (a), Ir L_3-edge (b) and Au L_3-edge (c) for the respective metal-functionalized UiO-67 MOFs, the spectra collected on MOFs are reported as orange and red colored lines (ppydc linkers), while the precursors are reported in grey.

3.1. Determination of the Rh Local Environment in Rh-UiO-67 MOF

XANES does not reveal a significant energy shift of the absorption edge for the Rh-UiO-67 sample with respect to the one of the precursor salt. This evidence suggests that the Rh-complex grafted in the MOF shows the same Rh oxidation state of the precursor salt, i.e. 3+. With respect to EXAFS analysis, the fits achieved for modulus and imaginary part of the Fourier Transform are reported in Fig. 2a. The fits are in a good agreement with the experimental spectra. In the UiO-67-Rh, the contributions of Rh-Cl and Rh-N single scattering paths are indicated with green and cyan lines, respectively, and they evidence the presence at shorter distances of two N atoms of the bpydc unit, while three Cl neighbours are located at longer bond distance from the Rh centre. However, it is well known that Rh(III) complexes prefer octahedral coordination. In the present case, the presence of an additional low-atomic-number atom (e.g. from a water or DMF solvent molecule) in the first coordination shell of Rh also results in satisfactory fit of the EXAFS spectra, within the available data quality (fit not reported). All the parameters refined in the fits, are reported in Table 1, where the underlined values have been fixed in the fitting procedure.
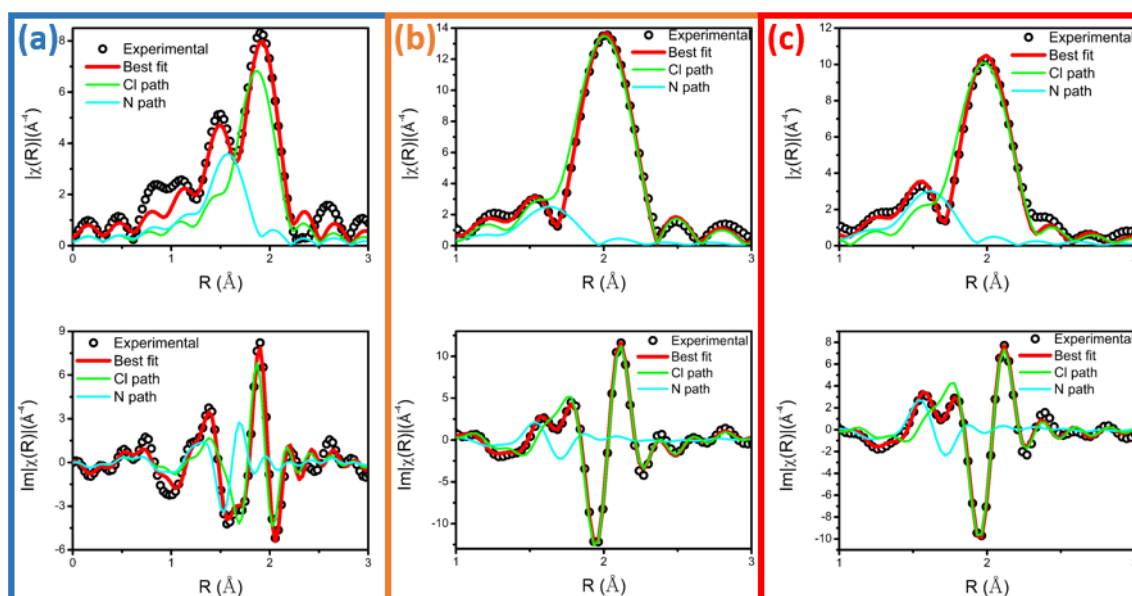

Figure 2. (a) Fourier transform of the experimental EXAFS spectra (black dots) and its best fit (red) of UiO-67 bpydc-Rh in modulus (top) and imaginary part (bottom); (b) and (c): same as (a) for UiO-67-Ir MOFs with bpydc (b) and ppydc (c) chelating linkers respectively. The SS paths involving Cl and N shells are shown as green and cyan solid lines, respectively.

3.2. Determination of the Ir Local Environment in Ir-UiO-67 MOF

The Ir-L_3 edge XANES spectra (Figure. 1b) of the two Ir-UiO-67 MOFs show a slight shift at higher energy (ca. 1 eV) and they show a significant increase of the white line intensity, compared the one of the $IrCl_3$ precursor. This evidence suggests a decrease in the electron density in the d orbitals on the metal center with respect the $IrCl_3$ precursor [3,7]. A similar behaviour has been observed for the UiO-67-bpy-Pt [3]. In Table 1 we observe that the experimentally refined coordination number for the Ir-Cl shell are (4.8 ± 0.3) and (3.5 ± 0.2) for MOFs with bpydc and ppydc linkers, respectively. In the case of Ir bpydc, we observe that the coordination number refined in the fit for N is less than two, suggesting the presence of some Ir sites not grafted to the MOF framework. The simplest alternative, supported also by the rather high Ir-Cl coordination number found, is the presence of a certain fraction of unreacted precursor salt $IrCl_3$ ($N_{Cl} = 6$) trapped in the MOF cavities. With this respect, we estimated roughly the percentage of grafted Ir-sites over the total number of Ir absorbers, and thus the percentage of salt that did not react. We used the system showed below Eq. (1), where N_{exp} is the coordination number obtained from the fit, N_{the} is the coordination number expected for Cl or N, x is the weight factor of N_{the}, y is the

weight factor of the precursor and N_{salt} is the coordination number of the salt (N_{salt} (Cl) = 6, N_{salt} (N) = 0 octahedral coordination).

$$\begin{cases} N_{exp} = \frac{(N_{the} \cdot x) + (N_{salt} \cdot y)}{x+y} \\ x + y = 1 \end{cases} \qquad (1)$$

Using the Ir-Cl coordination number, the estimated fraction of unreacted $IrCl_3$ is 0.4 ± 0.1 (0.25±0.08 using the Ir-N coordination number) for the MOF with bpydc linkers.

With respect to the UiO-67-Ir-ppydc, Ir(III) is well-known to form N,C-chelating complexes with ppydc type ligands by orthometalation process [8]. The experimentally refinement coordination number for the Ir-N/C shell is compatible with 2 within experimental error while for Ir-Cl shell is (3.5 ± 0.2). This suggest that the orthometalation process occurred in a majority of Ir sites. In addition, the Ir coordination sphere most likely include also three chlorine neighbours and possibly one solvent ligand (minorly contributing to the EXAFS signal as previously discussed for Rh) to complete the octahedral configuration. The charge in these metal complexes immobilized on the linker could be balanced by possible counter-ions present in the cavities and located at distances typically higher than 5 Å in a disordered configuration. Thus their identification by EXAFS is very difficult: future experiments using a third generation source and high k data collection would be required to further clarify this point, as well as to precisely locate possible solvent molecule coordinated to the metal center.

Table 1. Best fit parameters for $RhCl_3$ and $IrCl_3$ precursor salts and M-UiO-67 MOFs (M = Rh, Ir and Pt from [3]). The parameters fixed in the fit are underlined. The S_0^2 and σ_{Cl}^2 values have been chosen from the EXAFS fit of metal salt references, while the σ_N^2 values have been estimated on the basis of the analysis previously performed on the Pt-UiO-67 system [3].

Sample	Shell	N	$\sigma^2(Å^2)$	R(Å)	E_0(eV)	S_0^2	R-factor
$RhCl_3$	Rh-Cl	<u>6</u>	0.0038±0.0004	2.331±0.003	0±1	0.97±0.06	0.008
UiO-67-Rh	Rh-N	2.1±0.7	0.003	2.02±0.02	2±4	<u>0.97</u>	0.02
	Rh-Cl	2.5±0.2	<u>0.0038</u>	2.32±0.01			
$IrCl_3$	Ir-Cl	<u>6</u>	0.0038±0.0005	2.35±0.01	12±1	0.75±0.06	0.01
UiO-67-Ir (bpydc)	Ir-N	1.5±0.5	0.003	1.98±0.01	12±2	<u>0.75</u>	0.008
	Ir-Cl	4.8±0.3	<u>0.0038</u>	2.36±0.01			
UiO-67-Ir (ppydc)	Ir-N/C	1.7±0.4	0.003	1.99±0.01	9±1	<u>0.75</u>	0.01
	Ir-Cl	3.5±0.2	<u>0.0038</u>	2.35±0.01			
UiO-67-Pt	Pt-N	2.0±0.3	0.002±0.001	2.02±0.01	1±2	<u>0.92</u>	0.02
	Pt-Cl	1.8±0.2	0.0025±0.0006	2.295±0.008			

4. Conclusions and acknowledgements

XAS has proved PSF as a good method for chelating some metals, a part from Au, to the MOFs linkers, even though the efficiency can still be improved. The EXAFS experiments performed at third generation synchrotron could lead to a more precise comprehension of the presence of possible trapped solvent or other molecules in the MOFs and to solve the local structure around metal grafted to the linker with better accuracy.

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