Experimental report

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and long term persistence, even at very low concentrations. Among the currently applied technologies, adsorption is one of the most interesting ones to remove heavy metals due to its low energy consumption, easy applicability and re-usability, but classic adsorbents lack the required metal ion specificity. Metal Organic Frameworks (MOFs) have emerged as highly promising alternative to classic porous materials, especially to address heavy metal pollution. Due to the MOF´s chemical tuneabily they can be easily post-synthetically functionalized. In this proposal we aim to study the heavy metal adsorption and degradation mechanisms in amino acid modified MOF-808 material by means of inelastic neutron scattering experiments.

EXPERIMENT N°: 7-05-524

TITLE: Inelastic Neutron Scattering insight on metal adsorption mechanisms of natural amino acids modified Metal Organic Frameworks

REPORT 03/10/2022

Metal Organic Frameworks (MOFs) have emerged as promising microporous ordered materials for metal ion immobilization purposes, since MOFs have overcame the kinetics and adsorbing capacities over heavy metals reported for classic adsorbents. MOF-808, a water stable Zr-MOF, shows excellent adsorption capacities to oxyanions such as $CrO_4^{2^-}$, but little affinity to other metal cations, which can be overcome by decorating the pores with different functional groups. In this regard, we have incorporated histidine and cysteine amino acids into the pore of MOF-808 to endow the structure with different functional groups that increase the affinity towards different metal cations.

As a first attempt, infrared and Raman spectroscopy were used to observe the variations induced by the amino acid functionalization, and the posterior metal adsorption. Nevertheless, the signals associated to the amino acid molecules where highly weak, and no significant changes were observed after the metal immobilization. Inelastic neutron scattering (INS) data was a must to reveal the spectroscopic signals associated to the hydrogen atoms of amino acid molecules installed into the MOF-808. The obtained results have been divided in two different publications: one for the Cysteine modified MOF that has already been accepted in Chemistry of Materials, and a second one for Histidine modified MOF that will be submitted in the following weeks.

At a first step, the vibrational bands of the INS data of MOF-808, cysteine and MOF-808@Cys samples were identified on the basis of the bibliographic data. Two are the main spectral variations observed when the cysteine is anchored to the MOF (Figure 1a): (i) the vibrational modes of COOH and NH₃ disappear, and (ii) the bands associated to the CH, CH_2 , and the bending and rocking modes of SH and NH₃ groups, respectively, gain intensity in comparison to the ones of the free cysteine. It is important to note that the signals associated to the bending and rocking modes of SH (~ 975 cm⁻¹) and NH₃ (~ 990 cm⁻¹) groups in free cysteine molecules seem to be shifted to the same position in the MOF-808@Cys compound (~ 975 cm⁻¹). The disappear of the COOH vibrations (CO₂ rock at ~500 cm⁻¹) is in good agreement with the anchoring of the Cys molecules to the zirconium clusters of the framework via the carboxyl groups.

Among the INS bands affected by the metal adsorption (Figure 4.17b), the intensity of the signal located at 950 cm⁻¹ energy is slightly reduced in comparison to the initial MOF-808@Cys. The band was initially assigned to the combination of the bending vibration of SH and the rocking vibration of NH₃ groups. In addition to the subtle intensity loss, Pb^{II} and Cu^{II} adsorption induces a slight displacement of the signal to higher energy values. The metal coordination by sulfide groups by Cu^{II} or Pb^{II} ions would induce a deprotonation to S⁻ anions, and thus, to a reduction of the INS signals associated to the SH vibrational modes (~950 cm⁻¹). In contrast, as revealed by many metal-coordination complexes found in the CSD database, the coordination of NH₃ groups to Cu^{II} or Pb^{II} usually induces a deprotonation of the ammonium to amine, so the vibrational modes associated to NH₂ functions are still active after the metal complexation, although maybe displaced to a slightly different energy values.

On the other hand, the installation of Histidine molecules into the MOF induces the disapearence of the INS bands associated to the COOH vibrations (CO₂ rock usually located around ~500 cm⁻¹) (Figure 1c). As reported in several structral models determined by syngle crystal X-ray diffraction, this variation agrees with the coordination of the His molecules to the zirconium clusters via the carboxyl groups. In addition, the disappearance of the NH₃⁺ torsion vibration (usually shown for amino acids close to 300

cm⁻¹), points that the intermolecular interactions between His molecules once installed into the MOF-808 can block or mitigate this vibration. Among the INS bands affected by the metal adsorption (Figure 2), the most significant change is associated to the complete suppression of the mode associated to the skeletal vibration of the histidine molecules (~ 350 cm^{-1}) and the torsion vibrational model of NH₃⁺ groups. This can be easily understood, since independently on the single or cooperative mechanisms of the histidine molecules to coordinate copper ions, the mobility of the molecules installed within the MOF-808 pore space may be severely restricted once copper ions are directly linked to them.

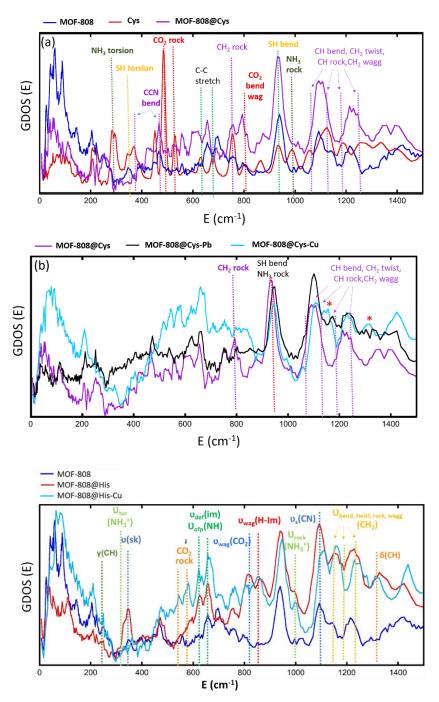


Figure 1. Inelastic scattering spectra of (a) MOF-808, L-Cysteine and MOF-808@Cys, (b) MOF-808@Cys after Pb^{II} and Cu^{II} adsorption and (c) MOF-808, MOF-808@His and MOF-808@His after Cu^{II} adsorption