

Experimental report

25/10/2022

Proposal: 7-05-524

Council: 4/2020

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

Research area: Chemistry

This proposal is a new proposal

Main proposer: Jose Maria PORRO AZPIAZU

Experimental team: Ainara VALVERDE DE MINGO
Natalia Ahiova RIO LOPEZ

Local contacts: Monica JIMENEZ RUIZ

Samples: MOF-808@Cysteine
MOF-808@Cys:Metal
MOF-808
Cysteine

Instrument	Requested days	Allocated days	From	To
IN1	6	4	17/02/2021	21/02/2021

Abstract:

Mining and industrial activities are continuous heavy metal pollution sources of water basins; which have a high environmental impact 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 tuneability 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.

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INSTRUMENT: IN1-LAGRANGE

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REPORT 03/10/2022

Metal Organic Frameworks (MOFs) have emerged as promising microporous ordered materials for metal ion immobilization purposes, since MOFs have overcome 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 were 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 NH_3 disappear, and (ii) the bands associated to the CH, CH_2 , and the bending and rocking modes of SH and NH_3 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 ($\sim 975 \text{ cm}^{-1}$) and NH_3 ($\sim 990 \text{ cm}^{-1}$) groups in free cysteine molecules seem to be shifted to the same position in the MOF-808@Cys compound ($\sim 975 \text{ cm}^{-1}$). The disappearance of the COOH vibrations (CO_2 rock at $\sim 500 \text{ cm}^{-1}$) 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 NH_3 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 ($\sim 950 \text{ cm}^{-1}$). In contrast, as revealed by many metal-coordination complexes found in the CSD database, the coordination of NH_3 groups to Cu^{II} or Pb^{II} usually induces a deprotonation of the ammonium to amine, so the vibrational modes associated to NH_2 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 disappearance of the INS bands associated to the COOH vibrations (CO_2 rock usually located around $\sim 500 \text{ cm}^{-1}$) (Figure 1c). As reported in several structural models determined by single 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 NH_3^+ torsion vibration (usually shown for amino acids close to 300

