Pressure response of the metal-organic framework MIL-101 filled with metal nanoparticles

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Metal–Organic Frameworks (MOFs) form a versatile class of porous crystalline hybrid materials where metal ions are connected by organic ligands. Due to the large variety of metals and organic linkers that can be used, MOFs have a large physical and chemical tunability. This allows the design of specific nanometer-scale framework geometries with desired pore structures. For these reasons, MOFs have represented so far the ideal materials for a large number of applications such as gas storage, gas/liquid separation, drug delivery, catalysis, etc [1].

Their tunable and porous nature makes these materials suitable for confining nanometric objects. The insertion of guest nanoparticles (NPs) within porous MOFs represents an effective way to stabilize them and fine-tune the functionality of the host [2]. The porous host can interact with the confined particles due to chemical bonding and steric effects. This interaction can be altered by an external pressure by modifying the balance between weak (i.e. Van der Waals) and strong (covalent) interactions and modify the overall surface-to-volume ratio, thus modifying both the chemical reactivity and the mechanical properties [3].

Among all the MOFs, the mesoporous chromium(III) terephthalate MIL-101 has a rigid zeotype crystal structure with two types of quasi-spherical cages, with pore diameters close to 29 and 34 Å [4]. Recently, we have successfully embedded Pd NPs with an average diameter of 1 nm (around 30-40 atoms per cluster) into MIL-101 (see Fig.1), for the first time with high metal loadings, up to 20 wt% (i.e. the Pd to sample mass) [5].

Here, we investigate the effect of high pressure on empty MIL-101 and x-Pd@MIL-101with 5 – 20 wt% by synchrotron based x-ray diffraction (XRD) and infrared (IR) spectroscopy in the 0-10 GPa pressure range. To the best of our knowledge, this is the first time the a mesouporous MOF such as MIL-101 is studied at high pressure. Although the large pore diameter, empty MIL-101 shows a high structural stability under compression with the lack of amorphisation in the pressure range explored, although signs of disorder and strain are detected. IR measurements show that the vibrational modes of the organic linker are still present up to 10 GPa, thus confirming the endurance of the molecular structure.

From a preliminary analysis, the presence of Pd nanoparticles inside the pores of the MOF does not have drastical effects besides changing the compressibility of the host framework.

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