

# **Effect of the metal on the gas-induced flexibility of sodalite zeolitic imidazolium frameworks (cobalt and zinc)**

**PROPOSAL CODE 25-01-1006**

**15<sup>th</sup> -19<sup>th</sup> February 2017**

## **Summary and objectives**

In previous proposals (25-01-942 and 25-01-965) we initiated a research based on exploring the gas adsorption induced structural transitions of nanoporous materials at different gas loadings at cryogenic temperature.

In collaboration with the powder diffraction station of the Spline at ESRF we constructed a novel set-up for in situ solid-gas processes in an isobaric and isothermal environment that allows the control of temperature, gas dosage and simultaneous HRPD recording at cryogenic temperature [1]. Using this set up, it was possible to study the direct structural phase transitions in a Metal Organic Frameworks (MOFs) and Zeolitic Imidazolium Frameworks (ZIFs) by the adsorption of various gases such as N<sub>2</sub>, Ar, O<sub>2</sub> or CO.

The main objective of this proposal was to extend the study analyzing the influence on the gas-induced structural transformations of the metallic ions (d<sup>7</sup> vs d<sup>10</sup> for cobalt and zinc, respectively) considering that they are easily accessible in the host (open metal sites).

## **State of the art**

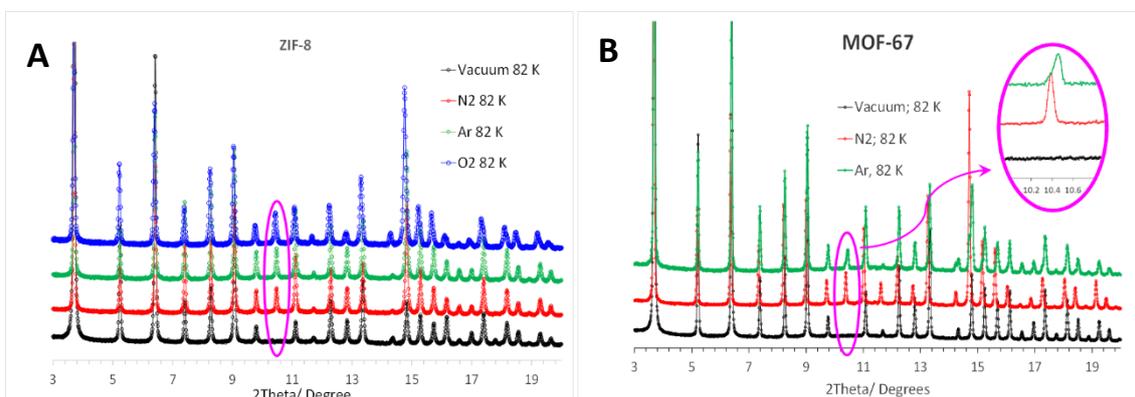
Porous coordination polymer networks (PCPs) have emerged as a new class of porous materials with improved properties compared to classical species (i.e zeolites, carbon adsorbents and oxides). A small group of such nanoporous materials have revealed rather unique structural flexibility not commonly associated with crystalline solids. Adsorption and diffusion of gas probes with kinetic diameters larger than the dimensions of the pore aperture of the solid have confirmed the flexibility in these structures. In this sense, our previous works on ZIF-8, that is a prototypical representative of the family of zeolitic imidazolium solids, revealed that the host flexibility seemed controlled by the packing arrangement of the gas inside the pores, and the polarizability and molecular size and shape of the gases [2-6]

ZIF-8 is based on the coordination flexibility of Zn (II) ions, on the other hand MOF-67 displays an isomorphic structure to ZIF-8, being Co (II) the metal ion bonding the imidazolium ligands (instead of Zn). The high resolution gas adsorption data of MOF-67 has also revealed similar singular adsorption features than ZIF-8, in terms of expansion of the total pore volume upon gas dosing compared to ZIF-8. Based on this, the aim of this study was to further analyses this behavior, trying to evaluate the effect of the metallic ion (i.e., Co and Zn) of the framework on the adsorption features of these compounds.

## Results

We have performed in-situ measurements of the X-ray diffraction patterns of both materials upon high vacuum and controlled gas adsorption ( $N_2$ ,  $O_2$  and Ar) at cryogenic temperature (i.e., 82 K). First, the samples need to be carefully outgassed under vacuum for at least 12 h (ideally overnight) and at ca. 120°C, to clean the structure before the gas dosages. Then, the spectra of ZIF-8 were recorded under varied loading conditions; although this material had been measured in former proposals, this protocol has allowed us to check both the experimental set-up and the protocol (Figure 1A). The obtained spectrum of ZIF-8 under high vacuum at 82 K in a  $2\theta$  range of 3-63° was in good agreement with those previously measured and reported in the literature for the diffraction pattern of the clean structure (before any gas-induced transition). Subsequently, the gases were dosed inside the nanoporous sample at saturation pressure (ca. 700 torr for all of them). The diffraction patterns obtained revealed the appearance of a new peak around 10.45 degrees (regardless the nature of the gas) indicating the occurrence of a gas-induced transition when  $N_2$ , Ar and  $O_2$  are dosed and adsorbed in the nanoporous cages of this material.

The same experimental procedure was followed to study the behavior of MOF-67, registering the HRPD spectra under high vacuum and dosing  $N_2$  and Ar at 82 K. The obtained patterns indicate a similar gas-induced transformation in the Cobalt-ZIF, as in the case of ZIF-8, with the peak at 10.45° in the loaded structure (Figure 1B). Thus it seems that the nature of the metallic center does not affect the packing of the structure of the gas; it may be concluded that the presence of open metal sites of metallic ions of different electronic structure ( $d^7$  vs  $d^{10}$ ) has a low impact on the formation of the zeolitic imidazolium structure upon gas adsorption. The effect would seem to be exclusively associated to the size of the nanoporous cavities (similar in both structures). Further analysis of the obtained data, including Rietveld refinement are ongoing to confirm the spectroscopic data.



**Figure 1.** High resolution synchrotron XRD patterns measured in **A)** ZIF-8 and **B)** MOF-67 at 82 K and various gas loading conditions: vacuum (black line, bottom) and saturation conditions (ca. 700 torr) of  $N_2$  (red line), Ar (green line),  $O_2$  (blue line, top).

## Scientific impact of the results obtained in this proposal

The outcome of this work is expected to be published in the forthcoming year; we also expect to present several contributions to international conferences on the fields of adsorption of nanoporous materials (i.e., meeting of the Spanish Association of Synchrotron Users to be held in Madrid 2017).

## References

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