

Real time monitoring of structural changes upon gas adsorption/desorption on Pd-based MOFs
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Summary and Objectives

Recently, in collaboration with the Spanish CRG at ESRF we have designed and used a cell that allows the real time monitoring of these structural transformations on the rigid zeolitic imidazolium framework (namely ZIF-8) under controlled conditions by monitoring the HRXRD during the gas dosage of the nanoporous material [1]. The measurement cell allowed the fine control of the gas dosage, sample outgassing in vacuum, temperature control and simultaneous HRPD recording. The pressure and temperature of the sample were controlled from 0 to 800 torr and 85 K.

In this proposal we aim to expand this study to a different family of materials that have also shown anomalous gas adsorption behavior upon equilibrium gas adsorption/desorption. Thus the objective of this proposal was to comprehend the anomalous gas adsorption behavior upon equilibrium gas adsorption/desorption of Pd-based porous coordination polymeric (PCP) materials by performing the structural analysis of the materials in-operando during the gas adsorption at cryogenic temperatures.

State of the art and background

In a previous study we reported the synthesis and characterization of the gas adsorption features of a family of porous thermally robust frameworks based on Pd and functionalized ligands (5-X-2-hydroxypyrimidine, with X =H or F for Pd-H or Pd-F samples, respectively), showing among other features, permanent porosity with high thermal stability and framework versatility [2,3]. These represented the first Pd(II)-based PCP (Figure 1), showing 3D microporous sodalitic networks and displaying promising features for gas adsorption and separation (ca. unusually high H₂ storage density at ambient pressure and cryogenic temperatures) [4]. The synthesis of these Pd-based MOFs implied a self-assembly process of metal fragments and organic spacers, which is facilitated by the use of labile metal ions, obtaining stable, discrete polynuclear systems, with nanosized voids. Both samples (Pd-F and Pd-H) crystallise in the cubic space group Pn3m, where the square planar Pd (II) ions -ca. 5.7 Å° apart- are connected through N1,N3-exobidentate X-pymo bridges. The presence of the ligands' bridging defines three different structural motives, namely, planar molecular hexagons, metallacalix[4]arenes and metallacalix[6]arenes, which interlock to build a 3D open framework of the sodalite zeotype. The presence of the fluorine substituent on the pyrimidine ring implies ca. 2.5% loss in the accessible empty volume of Pd-F with respect to Pd-H, as well as ca. 7% shrinkage of the b-cage radius (4.35 vs. 4.65 Å°, calculated as the distance between the centre of the cavity and the nearest atoms).

As for the adsorption features, the equilibrium N₂ adsorption isotherms at 77K showed outstanding differences between the samples (Figure 1). The isotherms displayed a type I-IV hybrid shape isotherm, with a type H1 hysteresis loop at relative pressures above 0.8, which is attributed to capillary condensation in interparticle mesopores (voids). Fluorine functionalisation does not have an effect on the surface area (ca. 600 m²/g for both materials); however, the isotherm of sample Pd-2F exhibited a singular upward step located at relative pressures between 0.01 > p/p₀ > 0.05, along with a hysteresis cycle in the desorption branch at the same relative pressure range (not seen

in the Pd-2H counterpart). The origin of this unusual behavior has not yet been clarified and various hypotheses have been proposed: i) pore blocking effects exerted by the fluorine residues of the b-cage hexagonal windows defined by the metallacalix[6]arene (Figure 1); ii) “breathing” or “swelling” effects in the flexible framework of the PCP [2,3]; iii) a phase transition in the nitrogen adsorbate; iv) the presence of defects in the crystals. To further clarify this issue and to confirm this hypothesis, we performed the synchrotron HRXRD patterns in operando during the gas adsorption at cryogenic temperatures.

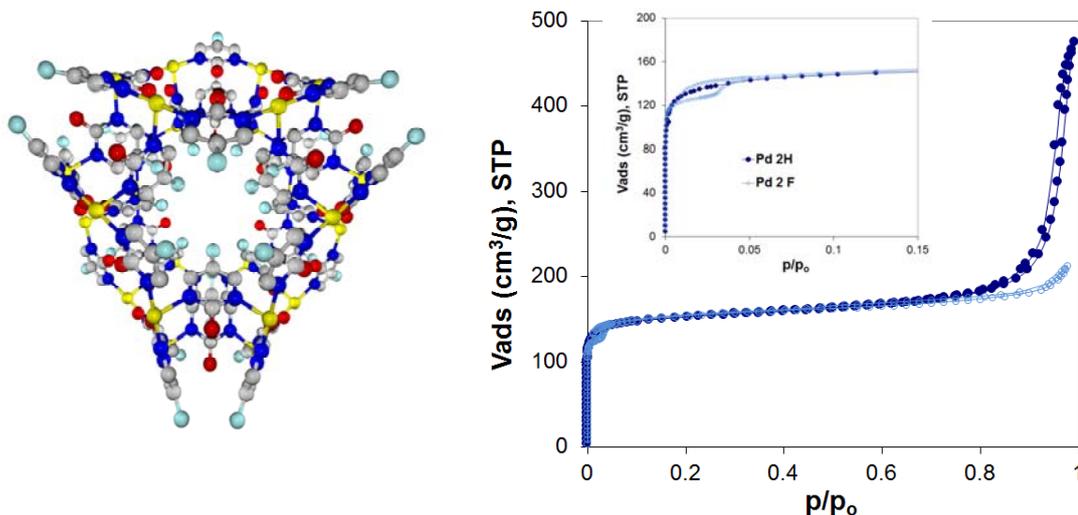


Figure 1. (left) Representation of the square-planar coordination environment of sample Pd-2F with the structural motives of the crystal structure (ca. blue light motives correspond to fluorine moieties, pointing towards inside the cage); (right) Nitrogen adsorption isotherms at 77 K of Pd-2F and Pd-2H (inset: magnification of the low pressure range to show the anomalous gas adsorption features).

Results

In our experiments, diffraction patterns of the samples were acquired at different gas pressures, from vacuum on the clean structure up to 800 torr of gas dosage (ca. atmospheric pressure) following a gas uptake pattern (adsorption), keeping isobaric and isotherm working conditions during data acquisition. We have used N₂ at 85 K, and we have compared the behavior with that recorded of a ZIF-8 material from our previous studies [1], for which we have observed gas-induced structural transitions (as an internal reference of the good performance of the in-situ cell and the in-operando procedure). It is important to remark that due to the large porosity of the samples, they need to be outgassed at least 12 hours at ambient temperature before recording the diffractograms (acquisition conditions were very strict, so as to have very high resolution patterns with 10 detectors simultaneously, measured in a 2θ range from 3° to 63° corresponding to a resolution better than 0.01 \AA). Also, the equilibration step with the gas at the different pressures requires at least 6 hours per gas pressure dosed.

Figure 2 shows as an example the diffractograms corresponding to the Pd-2F sample at 85 K under vacuum, and after loading at atmospheric pressure with nitrogen (several intermediates gas pressures loadings were also recorded). As seen, the HRXRD diffractograms of both experiments (vacuum and gas-loaded material) practically

overimpose over the whole range explored, suggesting that the saturated structure is similar to that under vacuum.

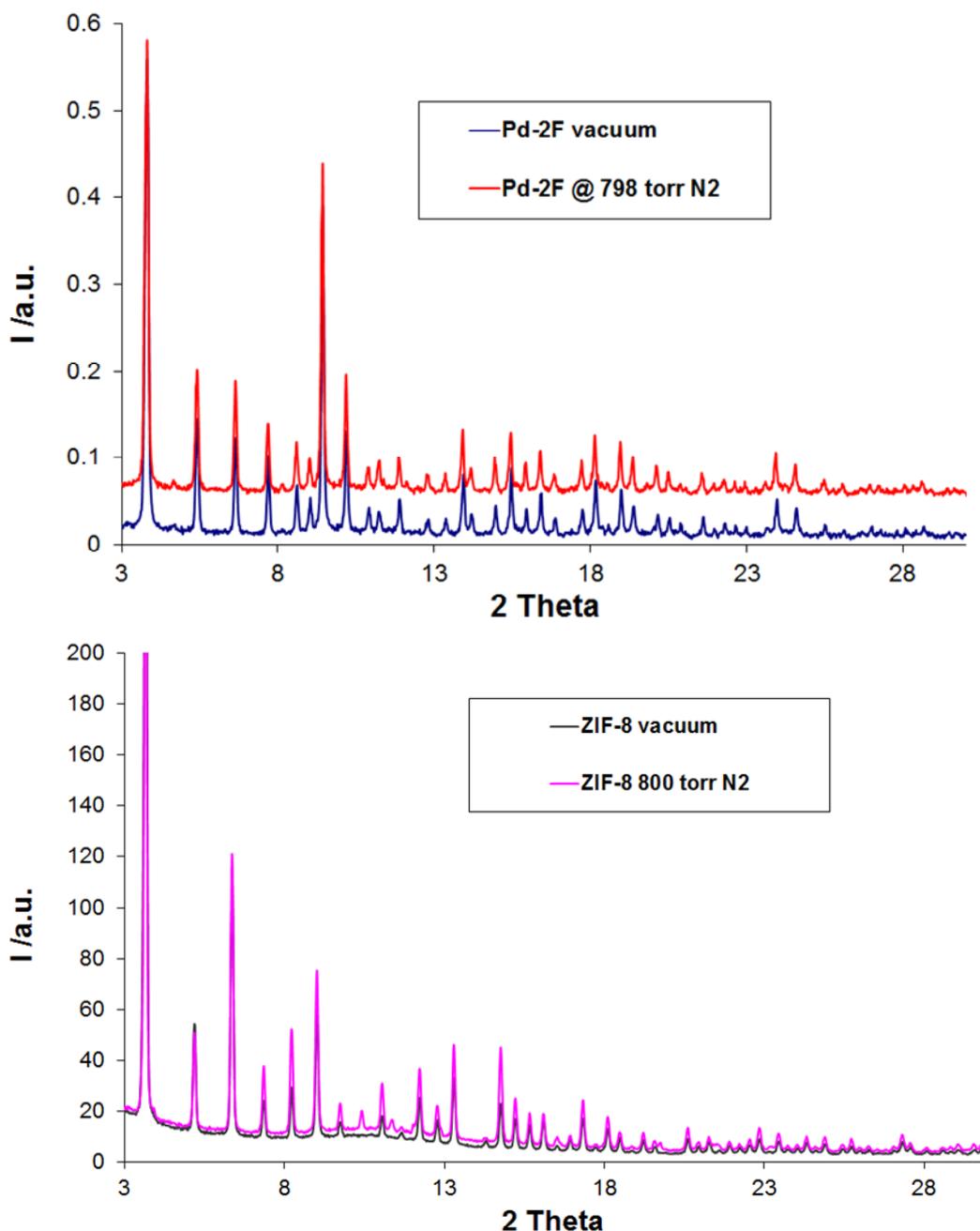


Figure 2. (top) High Resolution synchrotron X-ray diffraction patterns of Pd-2F at 85 K under vacuum and a gas loading of 800 torr. **(down)** Diffractograms of ZIF-8 at 85 K under vacuum and a gas loading of 800 torr.

A close analysis of the data revealed small differences with the appearance of small peaks at 12.2, 19.38 °; these are attributed to the appearance of ice during the cryogenic measurements (also visually observed outside the capillary), and thus cannot be assigned to the formation of new phases or to structural transitions in the material. In fact, we had observed the same effect in previous experiments and the refinement of the diffractograms confirmed that they are due to the formation of ice. Also, the gas-loaded patterns showed a slight but non negligible shift of the peaks towards low angles,

constrictions and difficulties in the accessibility of the gas inside the pore structure of the material due to the indicating a slight expansion of the cell upon the incorporation of the gas (hence a certain degree of flexibility of the material). Consequently, based on the HRXRD patterns, it may be inferred that the above-mentioned anomalous gas adsorption features of sample Pd-2F at cryogenic temperatures are most likely attributed to functionalization of the cages with the fluorine moieties pointed towards the center of the pore voids, rather than to a phase transition either of the adsorbate (nitrogen) or the framework (Pd-2F sample).

Comparatively, Figure 1 also shows the diffractograms corresponding to ZIF-8 (our internal standard used as a reference and verification of the correct operation of the in-situ cell system). The spectrum of ZIF-8 measured at high vacuum (after outgassing of the sample for 12 hours at room temperature) corresponds to the reported diffraction pattern of this material before the gas-induced transition [5,6]. Then, the reaction gas was dosed into sample at a saturation pressure (Fig. 1) and it was decreased until preselected fixed pressures to see the effect of gas desorption on the diffraction patterns.

In this sample, a new peak appears as the gas pressure is increased (ca. at 10.5°), due to the organization of the gas molecules in the small pockets of the material that are not accessible until the gas pressure reaches a threshold to induce the rotation of the methyl substituents of the material ligand [7,8]. Such direct in-situ evidences of structure deformation by the adsorption/desorption of the gases demonstrated that this set-up is perfectly suitable for direct structural analysis at in operando conditions [1].

SCIENTIFIC IMPACT OF THE RESULTS OBTAINED IN THIS PROPOSAL

We have explored the gas-induced phase transitions of Pd-based MOFs during gas uptake at equilibrium conditions and as a function of the gas properties, temperature and pressure, aiming at understanding the mechanisms governing the anomalous gas adsorption features reported in the literature for this material, and that had been attributed to several hypotheses.

The use of real time monitoring of the synchrotron HRPD patterns has enabled to discover the mechanism behind this behavior. The lack of changes in the diffractograms of the materials under vacuum (empty) and 800 torr (saturated with gas) at 85K has demonstrated that the differences in the gas adsorption features are due to pore constrictions hampering the access of the gas molecules in the structure rather than to gas-induced structural changes in the material upon dosing of the gas.

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. More details are as follows:

Gomis-Berenguer A, Parra JB, Salas-Colera E, Muñoz-Noval E, Garcia-Granda S, Castro GR, Barea E, Navarro JARM, Ania CO, Exploring the anomalous gas-adsorption of metal organic framework using in-situ synchrotron X-ray powder diffraction, (manuscript in preparation).

Bibliography

1. Calero S, Rubio-Zuazo J, Castro GR, Design and development of a controlled pressure/temperature set-up for in situ Studies of solid–gas processes and reactions in a synchrotron X-ray powder diffraction station, *J Synch. Radiation* 22 (2015) 42-48.

2. Navarro, JAR, Barea E, Salas JM, Masciocchi N, Galli S, Sironi A, Ania CO, Parra JB., H₂, N₂, CO and CO₂ sorption properties of a series of robust sodalite microporous coordination polymers, *Inorganic Chemistry*, 45 (2006) 2397- 2399.
3. Navarro JAR, Barea E, Salas JM, Masciocchi N, Galli S, Sironi A, Ania CO, Parra JB, Borderline Microporous-Ultramicroporous Palladium (II) Coordination Polymers. Effect of Pore functionalisation on Gas Adsorption Properties, *J. Materials Chemistry*, 17 (2007) 1-17.
4. Patent. Gas adsorbents based on microporous coordination polymers. WO/2006/134193 (ES200501561). Inventors: Rodríguez Navarro; Jorge A.; Salas Peregrín, Juan M.; Barea Martínez, Elisa; Masciocchi, Norberto; Galli, Simona; Sironi, Angelo; Parra Soto, José B.; Ovín Ania Concepción. Dates 10/06/2005 to 25/06/2025.
5. Gomis-Berenguer A, Muñoz-Noval A, Salas E, Para JB, García-Granda S, Castro GR, Ania CO, Structural deformation of ZIF-8 upon gas uptake and release gas adsorption at cryogenic temperature: a combined adsorption and synchrotron X-ray diffraction study, 2º Encuentro Iberoamericano de Adsorción, IBA-2, Cartagena de Indias, Colombia, 28-30 Abril 2015 (oral communication)
6. Parra JB, Garcia-Granda S, Castro GR, Calero S, Ania CO, Gas-induced structural deformation of ZIF-8: evidences by in-situ powder X-ray diffraction during gas adsorption, invited lecture presented in Workshop on Compliant Solids, 5-7 June 2013, Paris.
7. Ania CO, Parra JB, Haro M, Valdes-Solis T, García-Perez E, Calero S, Unravelling gas structural deformation of ZIF-8, *J. Phys. Chem. C*, 3 (2012) 1159-1160.
8. H. Tanaka, S. Ohsaki, S. Hiraide, D. Yamamoto, S. Watanabe, and M. T. Miyahara, *J. Phys. Chem. C*, 2014, 118, 8445.