Elucidation of CO_2 adsorption process in a bis-pyrazolate based MOF through HR-PXRD

S. Terruzzi[1], R. Vismara[2], S. Galli[2], V. Colombo[1]

[1]Department of Chemistry, University of Milan, via Golgi 19, 20133 Milan, Italy, [2]Dipartimento di Scienza e Alta Tecnologia, Università dell'Insubria, via Valleggio 11, 22100 Como, Italy

stephanie.terruzzi@unimi.it

Metal-Organic Frameworks (MOFs) are a class of synthetic porous crystalline materials based on metal ions connected through spacing ligands. They possess interesting properties such as high porosity [1], high concentration of metal centres and flexibility [2]. Additionally, MOFs can maintain their crystal structure upon removal, inclusion, exchange or reaction of a wide selection of guests, making them useful for multiple applications, *e.g.* in selective gas adsorption/separation. The synthesis of chemically and thermally stable MOFs, the comprehension of their properties and knowledge of their crystallographic features, are indispensable for the design and development of well performing materials. As MOFs' properties are intrinsically related to their crystal structure, a deep understanding of the *host-guest* interactions during adsorption processes is a fundamental aspect [3].

Here, a high-resolution powder X-ray diffraction (HR-PXRD) crystallographic study of the *host-guest* interactions in $Fe_2(BDP)_3$ [H_2BDP = 1,4-bis(pyrazol-4-yl)benzene] upon CO_2 adsorption is presented. This MOF is characterised by a 3D network with 1D triangular channels. The peculiar shape of its channels and its good Brunauer-Emmett-Teller specific surface area (1230 m^2/g) [4] prompted its investigation as CO_2 storage material, revealing an uptake capacity of 298.0 cm^3/g at P_{CO2} = 0.99 bar and T = 195 K.

At the ESRF ID22 beamline, HR-PXRD data were collected *in situ* and *operando* at T = 273 and 298 K while varying the CO_2 loading in the pressure range 0-8 bar. The obtained results will be presented after an in-depth data analysis, ranging from assessment of unit cell parameters variation to location of the primary adsorption sites and quantification of the adsorbed guest (Fig. 1). These results provide key information to better understand the *CO_2-host* interactions during the whole adsorption process, thus disclosing the chemical and structural features a MOF should possess to favour CO_2 uptake at mild conditions.

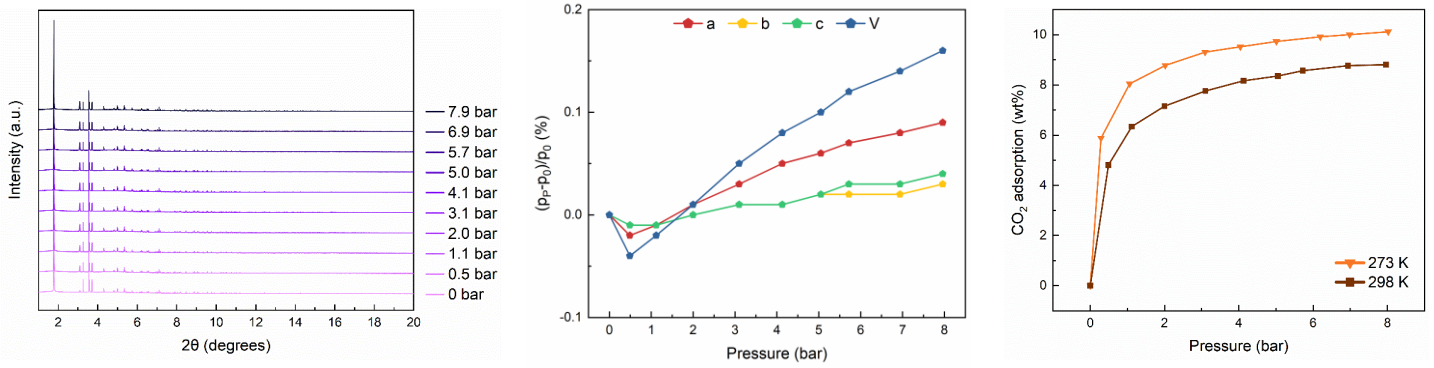

Figure 1. HR-PXRD patterns acquired at different CO_2 dosages and T=298 K (left); percentage relative variation of the unit cell parameters at T=298 K (centre); quantity of CO_2 adsorbed resulting from Rietveld refinement (right).

[1] I. M. Hönicke, I. Senkovska, V. Bon, I. A. Baburin, B. S. Raschke, J. D. Evans, S. Kaskel, *Angew. Chem.* **2018**, 57, 42, 13780-13783

[2] A. Schneemann, V. Bon, I. Schwedler, I. Senkovska, S. Kaskel, R. A. Fischer, *Chem. Soc. Rev.* **2014**, 43, 6062-6096; J. H. Lee, S. Jeoung, Y. G. Chung, H. R. Moon, *Coord. Chem. Rev.* **2019**, 389, 15, 161-188

[3] C. Giacobbe, E. Lavigna, A. Maspero, S. Galli, *J. Mater. Chem. A* **2017**, 5, 16964

[4] Z. R. Herm, B. M. Wiers, J. A. Mason, J. M. van Baten, M. R. Hudson, P. Zajdel, C. M. Brown, N. Masciocchi, R. Krishna, J. R. Long, *Science* **2013**, 340, 960-964

Keywords: MOF; CO_2 adsorption; synchrotron XRPD; host-guest interaction; Rietveld refinement.