

Experiment Report Form


Experiment title:

 Unveiling the CO₂ adsorption sites in the triangular channels of Fe₂(BDP-NH₂) metal-organic framework by in situ HR-PXRD

Experiment number:

CH-6073

Beamline: ID22	Date of experiment: from: 5 october 2021 to: 9 october 2021	Date of report: 11 March 2022
Shifts: 9	Local contact(s): Giorgia Confalonieri	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Simona Galli ¹ , Rebecca Vismara ^{*1} , Valentina Colombo ^{*2} , Stephanie Terruzzi ^{*2} ¹ Dipartimento di Scienza e Alta Tecnologia, Università degli Studi della Insubria, via Valleggio 11, 22100 Como, Italy. ² Dipartimento di Chimica, Università degli Studi di Milano, via Golgi 19, 22100 Milano, Italy		

Report:

Experiment CH-6073, performed at the ID22 High-Resolution Powder Diffraction Beamline, aimed to get information on the CO₂ adsorption properties of the MOF Fe₂(BDP-NH₂)₃ and Fe₂(BDP)₃ [H₂BDP = 1,4-bis(pyrazol-4-yl)benzene; H₂BDP-NH₂ = 1,4-bis(pyrazol-4-yl)amino benzene], which are isostructural metal organic frameworks characterised by a 3D network with 1D triangular channels. The peculiar shape of their channels and good Brunauer-Emmett-Teller specific surface area (1230 m²/g for the non-functionalized MOF) prompted its investigation as CO₂ storage material. Fe₂(BDP)₃ has been isolated and characterized in the recent past as *per* its crystal structure, textural properties (by means of N₂ at 77 K and CO₂ at 195 K) and performance in C₆H₁₄ isomers separation.[1] The isomorphous amino-tagged counterpart Fe₂(BDP-NH₂)₃ has been now prepared and fully characterized in the solid state in our labs, this including investigation of its porosity (through N₂ at 77 K and CO₂ at 195 K). As disclosed by PXRD, none of the two MOFs loses crystallinity or shows phase transitions after being probed with N₂ or CO₂. More interestingly, we have studied Fe₂(BDP)₃ and Fe₂(BDP-NH₂)₃ for CO₂ separation from N₂/CO₂ 85:15 binary mixtures (T = 273-353 K) and the breakthrough experiments showed that Fe₂(BDP-NH₂)₃ outperforms Fe₂(BDP)₃ in the studied conditions.

HR-PXRD *in situ* and *operando* measurements were performed working at 35 keV ($\lambda = 0.354 \text{ \AA}$, calibrated with the Si NIST standard SRM 640c at room temperature). Fe₂(BDP-NH₂)₃ was activated and introduced into a 0.5 mm-diameter borosilicate glass capillary in our lab prior to the experiment. The capillary was first aligned, then connected to the gas handling system. The sample was further activated at 453 K under vacuum ($\sim 10^{-6}$ bar) by means of a turbo vacuum pump for approximately 2 h. All the measurements were carried out on the same capillary, changing its position to avoid radiation damage; an equilibration time of 15 min was applied at each CO₂ pressure before acquiring the HR-PXRD data.[2] The latter were collected at T = 273 and 298 K, while varying the CO₂ loading in the pressure range 0-35 bar. Prior to CO₂ dosage, space group and unit cell parameters were validated performing whole powder pattern refinements (TOPAS-Academic V6) on the data collected at 0 bar at both temperatures. The high quality of the HR-PXRD data enabled us to perform the planned structural study at T = 273 and 298 K. The Fe₂(BDP-NH₂)₃ framework was built up starting from the ambient-conditions crystal structure published for the non-functionalized MOF [1] and refined with the Rietveld method working on the 0 bar data. The two independent ligands and the CO₂ molecule were modelled as rigid bodies. For both ligands, the presence of orientational disorder affecting the central phenyl ring was taken into consideration.

The primary CO₂ adsorption sites were located by means of the Simulated Annealing approach and then refined through the Rietveld method. Comparing the HR-PXRD data of Fe₂(BDP-NH₂)₃ upon CO₂ adsorption, neither loss of crystallinity, nor amorphization or phase transition were observed in the studied range of temperatures and pressures. A preliminary whole powder pattern refinement showed a first unit cell volume contraction in the CO₂ pressure range 0-1 bar, followed by a slight expansion ($\Delta V < 1\%$), both related to CO₂ loading. In order to localise and quantify the adsorbed CO₂, assessment of the guest position and orientation followed by Rietveld refinement is currently in progress. To now it can be show that three primary adsorption sites with different occupancy were invariably identified, irrespective of the essayed conditions. Interestingly, both at 273 and 298 K, the applied CO₂ pressure affects the degree of positional disorder featured by the central phenyl ring of one of the two independent ligands and of the amino groups interacting with the CO₂ molecules. The amount of CO₂ adsorbed increases applying higher pressures and it is inversely proportional to the adsorption temperature. Monte Carlo simulations are currently in progress to further strengthen the correctness of the experimental findings.

Our structural insight will provide key information to shed light on the chemical and structural properties a host should possess for efficient CO₂ adsorption and separation at rather mild conditions.

References:

- [1] 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.
- [2] M. Brunelli A. N. Fitch, *J. Synchrotron Rad.*, **2003**, 10, 337-339.