

Experiment Report Form



	Experiment title: The role of CO ₂ in modulating the speed of a molecular rotor inserted in a metal-organic framework	Experiment number: CH-5337
Beamline: ID22	Date of experiment: from: 18 July 2018 to: 22 July 2018	Date of report: 04 March 2021
Shifts: 9	Local contact(s): Mauro Coduri	Received at ESRF:
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-5337, performed at the ID22 High-Resolution Powder-Diffraction Beamline, aimed to get information on the role of CO₂ in tuning the performance of the ultrafast molecular rotor H₂BPEB [H₂BPEB = 1,4-bis(1*H*-pyrazol-4-ylethynyl)benzene] when introduced as a spacer in the crystal structure of a metal-organic framework (MOF) through *in situ* and *operando* high resolution powder X-ray diffraction (HR-PXRD) at different temperatures and CO₂ loadings, through the gas handling system described in [1]. During the experiment we took advantage of the same experimental set-up to study another MOF, namely: Fe₂(BDP)₃ [H₂BDP = 1,4-bis(pyrazol-4-yl)benzene], [2] which is characterised by a 3D network with 1D triangular channels. The peculiar shape of its channels and its good

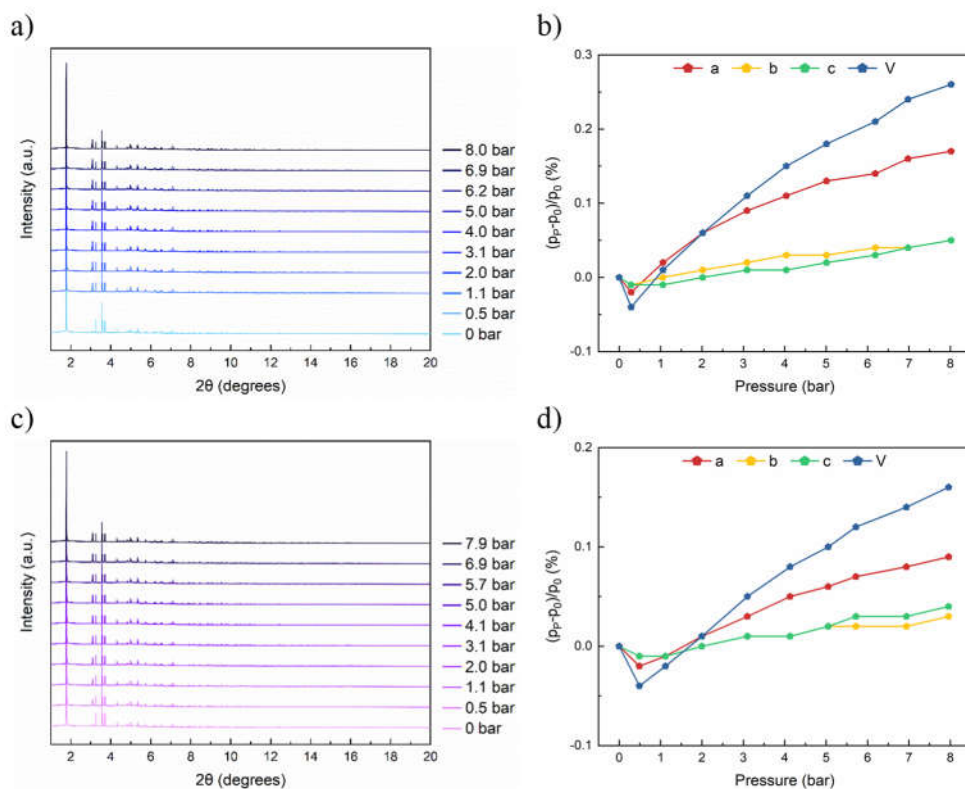


Figure 1. HR-PXRD patterns at different CO₂ dosage at 273 K (a) and 298 K (c) and percentage relative variation of the unit cell parameters at 273 K (b) and 298 K (d).

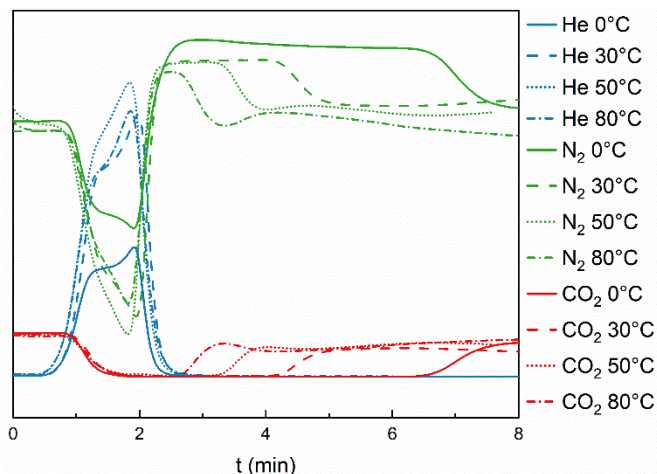


Figure 2. Breakthrough curves at different temperatures.

evidence of crystallinity loss. HR-PXRD *in situ* and *operando* measurements were performed working at 27.5 keV ($\lambda = 0.451 \text{ \AA}$, calibrated with the Si NIST standard SRM 640c at room temperature). $\text{Fe}_2(\text{BDP})_3$ 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 CO_2 pressure before acquiring the HR-PXRD data. The latter were collected at $T = 273$ and 298 K, while varying the CO_2 loading in the pressure range 0-8 bar. Prior to CO_2 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 framework was built up starting from the ambient-conditions crystal structure [2] and refined with the Rietveld method working on the 0 bar data. The two independent ligands and the CO_2 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 CO_2 adsorption sites were located by means of the Simulated Annealing approach and then refined through the Rietveld method. Comparing the HR-PXRD data of $\text{Fe}_2(\text{BDP})_3$ upon CO_2 adsorption (Figures 1a and 1c), 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 (Figures 1b and 1d) a first unit cell volume contraction in the CO_2 pressure range 0-1 bar, followed by a slight expansion ($\Delta V < 1\%$), both related to CO_2 loading. In order to localise and quantify the adsorbed CO_2 , assessment of the guest position and orientation followed by Rietveld refinement was successfully performed as detailed above. Three primary adsorption sites with different occupancy were invariably identified, irrespective of the essayed conditions. Interestingly, both at 273 and 298 K, the applied CO_2 pressure affects the degree of positional disorder featured by the central phenyl ring of one of the two independent ligands. The amount of CO_2 adsorbed increases applying higher pressures and is inversely proportional to the adsorption temperature (Figure 3). Monte Carlo simulations to further strengthen the correctness of the experimental findings are currently in progress.

Our structural insight will provide key information to shed light on the chemical and structural properties a host should possess for efficient CO_2 adsorption and separation at rather mild conditions.

References:

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

Brunauer-Emmett-Teller specific surface area ($1230 \text{ m}^2/\text{g}$) prompted its investigation as CO_2 storage material. Indeed, it was probed in CO_2 adsorption, revealing a CO_2 uptake capacity of $298.0 \text{ cm}^3/\text{g}$ at $P_{\text{CO}_2} = 0.99 \text{ bar}$ and $T = 195 \text{ K}$ [2]. Aiming at extending this work, we evaluated the $\text{N}_2:\text{CO}_2$ selectivity with breakthrough experiments, flowing a $\text{N}_2:\text{CO}_2 \sim 85:15 \text{ v/v}$ mixture through a column containing the activated MOF at different temperatures ($T = 273, 303, 323$ and 353 K , total gas flux = $20 \text{ mL}/\text{min}$). As a general trend (Figure 2), Fe_2BDP_3 can selectively adsorb CO_2 over N_2 with a CO_2 adsorption capacity inversely proportional to the acquisition temperature. Moreover, the separation process can be repeated at least 11 cycles ($T = 303 \text{ K}$, activation $T = 393 \text{ K}$ under He flux of $20 \text{ mL}/\text{min}$), with a slight performance loss, but no

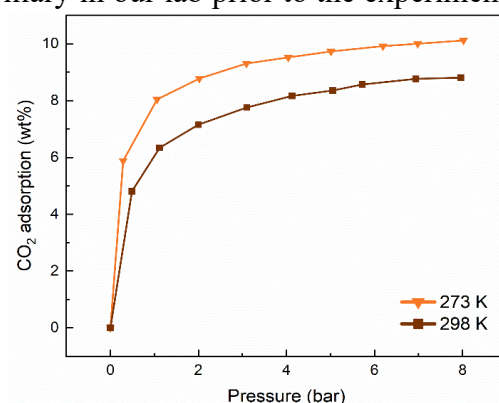


Figure 3. Quantity of CO_2 adsorbed resulting from Rietveld refinement.