Metal-Organic Frameworks: crystallographic explorations of porosity and functionality

V. Colombo[1]

[1]Dipartimento di Chimica, Università degli Studi di Milano, via Golgi 19, 20133 Milano (Italy)

Valentina.colombo@unimi.it

Understanding the adsorption properties of porous materials hinges on the ability to unravel their structural and electronic response to guest molecules. In particular, metal–organic frameworks (MOFs) offer a unique platform for designing materials with selective adsorption properties and tailored active sites. However, the role of coordinatively unsaturated metal centers, specific adsorption sites, and guest-induced structural dynamics often remains elusive.

In this lecture, I will present how our research leverages *in situ* and *operando* crystallographic and spectroscopic techniques - often in tandem - to uncover the structure–function relationships governing adsorption and catalysis in MOFs. By combining variable-pressure powder X-ray diffraction (PXRD), X-ray absorption spectroscopy (XAS), and custom-designed experimental setups, we gain simultaneous insights into both long-range order and local electronic/structural environments.

Recent studies will illustrate: (i) the in situ detection of preferential adsorption sites for CO_2 under humid conditions; (i) the combined use of PXRD and XAS to monitor structural evolution during gas uptake and surface defective sites; and (ii) a new approach to derive thermodynamic and structural parameters, such as the heat of adsorption and host–guest interactions, directly from PXRD-derived CO_2 isotherms via ab initio structure solution and Rietveld refinement.

These results demonstrate how an integrated, multi-technique approach can advance the understanding of responsive porous materials. and guide the design of next-generation adsorbents.

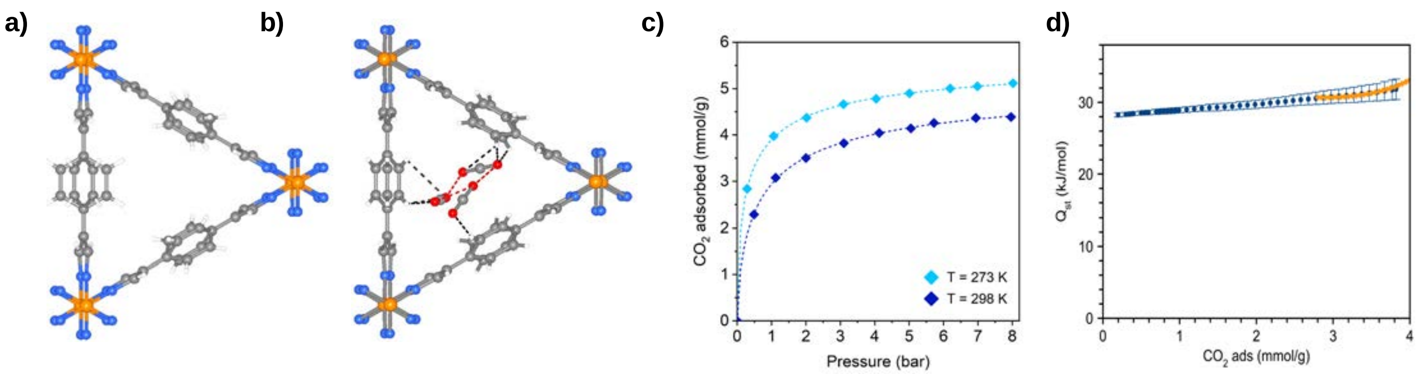

Figure 1. Structural response and adsorption behavior of FeBDP upon CO_2 loading revealed by Rietveld refinement: torsional flexibility, host–guest interactions, refined isotherms, and isosteric heat comparison.

[1] Vismara, R.; Terruzzi, S.; Maspero, A.; Grell, T.; Bossola, F.; Sironi, A.; Galli, G.; Navarro, J.A.R.; Colombo, V. (2024) *Advanced Materials*, **36**, 2209907

[2] Tofoni, A.; Tavani, F.; Vandone, M.; Braglia, L.; Borfecchia, E.; Ghigna, P.; Stoian, D.C.; Grell, T.; Stolfi, S.; Colombo, V.; D'Angelo P. (2023) *J. Am. Chem. Soc.* **145**, 38, 21040.

[3] Braglia, L.; Tavani, F.; Mauri, S.; Edla, R.; Krizmancic, D.; Tofoni, A.; Colombo, V.; D'Angelo, P.; Torelli, P. (2021) *J. of Phys. Chem. Lett.* **12**, 9182.