MS30 Advanced porous materials : MOFs, COFs, SOFs....and what else?

MS30-04

Pore architecture of the MIL-53(Al) mechanically controlled to intelligently modulate CO_2 adsorption

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Abstract

External control over the pore size of flexible Metal-Organic Frameworks (MOFs) such as MIL-53(Al) (MIL: Matériaux de l'Institut Lavoisier) has recently emerged as an innovative and promising concept, with possible applications to gas storage and separation [1]. In this work we have designed a new type of pressure cell capable of studying by in situ powder X-ray diffraction the structural behaviour of the MOF MIL-53(Al) under the combined application (i) of a mechanical stress ($\sigma_{mech} \leq 1$ GPa) and (ii) a gas pressure ($P_{gas} \leq 20$ bar). This new cell developed in collaboration with Almax-easyLab or "combined stress-pressure clamp" (CSPC) was successfully validated on the XPress line at Elettra Sincrotrone Trieste by following the structural modifications of MIL-53 (Al) which as it is well known presents different crystalline forms with variable volumes: (i) large-pore form (lp, $V_{uc} \sim 1450$ Å^3), narrow-pore form (np, $V_{uc} \sim 900$-1150 Å^3) under gas adsorption (CO_2, H_2O,...) and (ii) closed-pore form (cp, $V_{uc} \sim 890$ Å^3) only obtained by compression and stabilized by the π-π interactions between the benzene rings of the organic linkers in the wine-rack 1D porous network of the solid [2]. An excellent consistency of the switchabilty of the structure with previous work was demonstrated under uniaxial mechanical stress (Figure 1a) and then under CO_2 adsorption with the identification of the three possible forms of MIL-53(Al). When the two stimuli ($\sigma_{mech}+P_{gas}$) are combined, the results obtained show: (i) for the first time the reopening of the cp form of MIL-53(Al) towards the np then lp form and (ii) a dependence of the adsorption pressures leading to the formation of these forms with applied mechanical pressures (Figure 1b-d). This work has therefore allowed a better understanding of the interaction between mechanical stress and the adsorption of host molecules and thus opens the door to other opportunities for innovative applications, such as external control over separation performance, stress-swing adsorbent regeneration, actuated gas storage and fluid-solid barocaloric for example.

References

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Figure 1: Selected sweeps of P under increase σ