

Can a secondary control of materials structure be of interest for gas capture or storage ?

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Gas separation processes involving adsorption may have advantages over other separation methods although one drawback still remains the need for increased selectivity. A simple way to improve the selectivity of a separation process is to increase the pore confinement. One can modify materials via the inclusion of large cations in the case of zeolites or control the activation conditions of carbons. With flexible metal organic frameworks, one can modify the chemistry to control the pore size or shape. These methods can be considered primary controls of the pore structure. The question arises as to whether it is possible to control the pore size or shape during the adsorption process via a 'secondary' control.

In this fundamental study, we have applied an external pressure to compress a flexible MOF, MIL-53. Indeed, some MOFs (Metal Organic Frameworks) are considered as soft porous crystals which can change reversibly their structure when they are exposed to stimuli such as adsorbed molecules¹, pressure² or temperature. This structural flexibility, leading to a change in the pore size, strongly influences the selectivity of the adsorbent for some gas mixtures. For example, the MIL-53 solid in its narrow pore form exhibits a very good CO₂/CH₄ selectivity, which is lost when the structure switches to the large pore form with the increase of gas pressure³. By maintaining the narrow pore form via mechanical compression, it may be possible to control its selectivity over a wider range of pressure or even induce molecular sieving. Releasing the mechanical pressure will lead to the large pore form which could be easier to regenerate.

For this purpose, we have developed a novel methodology to tune the adsorption behavior of mechanically responsive materials by coupling the effects of 'internal' gas adsorption pressure and 'external' mechanical pressure. In order to pilot the structural flexibility of the adsorbent during the gas adsorption, we built an experimental device to apply a mechanical pressure (up to 25 tons) on the porous material via a uniaxial press system which equally allows gas adsorption up to 15 bars.

Results showing proof of concept with the MIL-53 will be given along with some openings towards more applied subjects.

References

- 1 S. Bourrelly, P.L. Llewellyn, C. Serre, F. Millange, T. Loiseau, G. Férey, J. Amer. Chem. Soc., 2005, 127(39) 13519-13521.
- 2 I. Beurroies, M. Boulhout, P.L. Llewellyn, B. Kuchta, G. Férey, C. Serre, R. Denoyel, Angew. Chem. Int. Ed., 2010, 49(41), 2010, 7526-7529.
- 3 L. Hamon, P.L. Llewellyn, T. Devic, A. Ghoufi, G. Clet, V. Guillerm, G.D. Pirngruber, G. Maurin, C. Serre, G. Driver, W. Van Beek, E. Jolimaître, A. Vimont, M. Daturi, G. Férey, J. Amer. Chem. Soc., 2009, 131(47) 17490-17499.