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In-situ control of soft adsorbents pore size for optimal separation properties

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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 in the adsorbent. For instance, this can be achieved by the inclusion of large cations in the case of zeolites or by controlling the activation conditions of carbons. With flexible Metal-Organic Frameworks (MOFs), one can modify the chemistry to control the pore size or shape. These methods allow a primary control of the pore structure from the synthesis step. However, the question arises as whether it is possible to control the pore size or shape of existing porous adsorbents during the adsorption process via utilization of an external stimulus.

In this fundamental study, we have applied an external mechanical pressure to compress a flexible Metal-Organic Framework, MIL-53. Indeed, some MOFs 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.

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