

Tailored-pore materials on polymeric membranes for gas separation

Separation operations in the chemical processes are the most energy and money consuming for the large industries and, therefore, one of the most important challenges for the chemical engineers to overcome now and in the next decades for the sake of a sustainable production and development in terms of efficiency and environmental care. Refining of pharmaceutical products, purification of effluents or natural gas cleaning, among other separation operations, are present in every chemical industry all over the world.

Traditionally the separation of mixtures of chemicals was carried out in huge distillation towers at extreme temperatures, which were energy and room consuming. However, the spreading on the use of membranes improved the efficiency of some of these processes: made by cheap polymeric materials, they can be shaped into tiny hollow fibers (0.5 mm in diameter) or spiral wounds, and are commercially applied in e.g. dialysis, reverse osmosis or nanofiltration. Therefore thousands of meters of membranes can be placed in small volumes: an area larger than a soccer pitch is folded to occupy just a cubic meter. Membranes act as barriers through which only the permeation of one of the components is favored.

Anyway, membrane features were not as great as desired because of the intrinsic trade-off between the productivity rate and the quality of the separation (called selectivity) achieved. To overcome this drawback, some nanomaterials can be added or deposited on the surface of the pristine membranes to drastically improve the membrane performances.

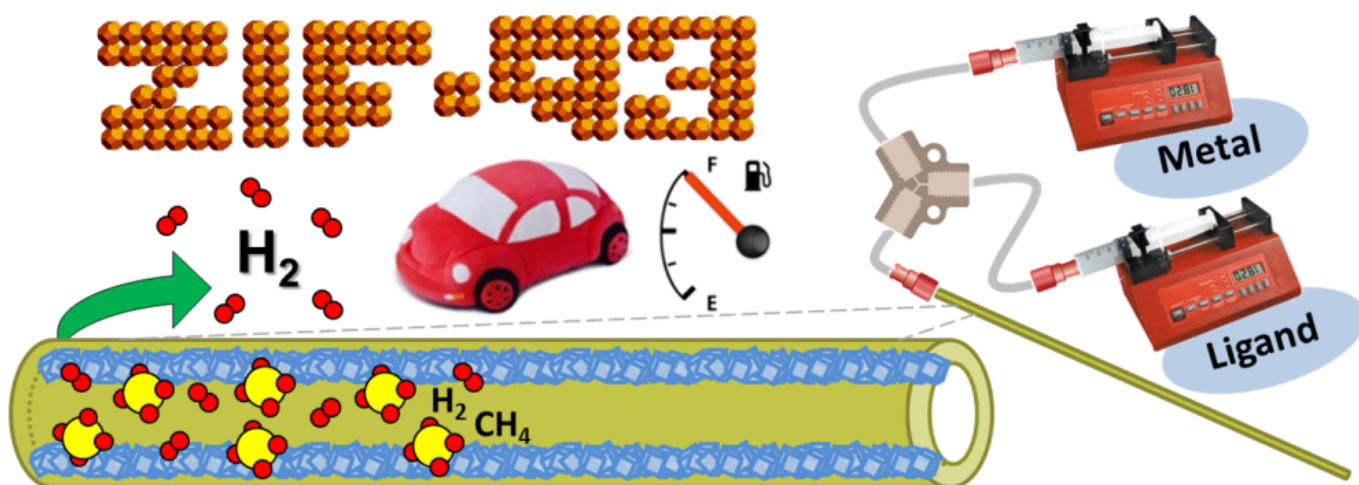


Fig. 1. ZIF-93 crystals growth inside a polymeric hollow fiber membrane selectively separate H₂ and CO₂ molecules from the larger CH₄. The ecofriendly fabrication by microfluidics minimizes the residue effluents.

Among the most promising, ZIFs (from zeolitic imidazolate frameworks) are powdered materials created from the reaction of metal salts and organic ligands at very soft conditions. They are mostly void, their atoms being crystalline ordered forming cavities regularly-sized in the order of a few Angstroms (Å, 5000 times smaller than a sand grain). In our work "*Highly selective ZIF-93 membranes inside co-polyimide P84 hollow fibers for gas separation*" published in [RSC Chemical Communications](#), ZIF-93 crystals were grown inside a polymeric hollow fiber creating a membrane. Only the smallest gas molecules (H₂ and CO₂ are 2.8 and 3.3 Å in size, respectively) were allowed to pass through their cavities (3.6 Å size) while the larger CH₄ ones (3.8 Å) were retained (see Figure 1). That is how a binary gas mixture can be split without any important energy input (except for the pressurization of the feed stream). 60 times H₂ molecules for each CH₄ one were able to pass through our membranes at 35 °C, and even almost 100 times more at 100 °C, which were all collected and analyzed in the gas streams afterwards. These gas flows enriched in H₂ could be afterwards used for H₂-vehicle feeding as petroleum alternative or for clean energy production. Similarly, CO₂-rich streams would be disposed so as to reduce the greenhouse effect in the atmosphere.

But this outstanding separation achieved is not the only advantage of the membrane fabrication method developed by our group. The use of small pumps that slowly push the reagents only along the inner volume of each hollow fiber drastically reduces the spending on hazardous chemicals and petroleum-derivate solvents, as compared with the previous alternatives present in the literature. This approach, known as [microfluidics](#), also allows to control some other fabrication parameters easily and reduces scale-up effects: our membranes could be tailored and sized as required in a simple manner and applied for different issues such as portable filling stations, control of flue gas emissions, etc.

To sum up, new materials with tailored characteristics and extremely narrow porosities, such as ZIFs, to be deposited on a cheap polymeric membrane, can lead to results never achieved before in the separation of gas mixtures of great interest for the chemical industry. These approaches will lead to a step-by-step intensification of the chemical processes regarding efficiency and environmental caring.

Publication

[High selectivity ZIF-93 hollow fiber membranes for gas separation.](#)

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