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1	Towards large-scale application of nanoporous materials in membranes for
2	separation of energy-relevant gas mixtures
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21	Abstract
22	Membranes containing nanoporous materials (such as zeolites, metal-organic
23	materials and 2D materials such as graphene derivatives) may allow more
24	efficient separation of gas mixtures relevant to emerging energy technologies.

25 For example, such membranes could be applied in the separation of gases

containing mixtures of carbon dioxide (CO₂) and hydrogen (H₂). However, these 26 27 membranes are currently at a relatively low technology readiness level. Hence, here we review the opportunities and challenges of applying these porous 28 29 materials in practice and at scale in membranes for possible commercialization. Besides, we highlight the necessity of improvements in the porosity control of 2D 30 materials and the decrease in the selective membrane skin layer when adapted 31 in asymmetric membranes. In this latter point, we declare the main limitation of 32 porous supports, as well as the further developments in the gutter layer and 33 supports. Additionally, we review the main membrane module configurations and 34 process requirements, declaring the most suitable configurations (e.g. spiral 35 wound and hollow fiber modules) at scale with promising future for highly 36 intensified membrane modules for applicability in CO2 and H2 separations. 37 38 Finally, apart from the conclusions derived from this review, we outline key recommendations for the researchers in the field. 39

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Keywords: Gas separation; porous materials; membrane modules; hollow fibers;
challenges; hydrogen separation; CO2 separation.

44 **1.** Introduction

As the world seeks to move to greener energy technologies and to lower carbon
footprints and emissions, a number of gas separation processes may become
more important. For example, gas mixtures related to energy production include
CO₂/N₂ (post-combustion carbon capture), CO₂/CH₄ (production of biomethane)
and H₂/CO₂ (pre-combustion carbon capture). Current gas separation technology
largely relies on thermally-driven processes, such as distillation, absorption and

adsorption. Yet, there is evidence that some membrane-based separations applying concentration and pressure gradients may be more energetically efficient and environment-friendly than existing processes, and they could limit carbon dioxide emissions and reduce costs [1].

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High-performance membranes for gas separation consist of a composite 56 structure in which, ideally, an ultrathin film based on selective materials is placed 57 on top of a mechanically robust porous support, constituting a thin-film composite 58 (TFC) membrane (see Fig. 1)[2]. As of now, gas separation membranes are 59 60 dominated by polymeric materials due to the fact that polymers can be rapidly processed into the TFC morphology. However, the gas separation performance 61 from the polymeric membranes is limited by the intrinsic properties of the polymer 62 63 determining gas sorption and diffusion, molecular solubility, the free volume between the polymeric chains, and chain stiffness [3-5]. Some of these 64 properties have been improved with the so-called next-generation polymeric 65 materials, e.g., polymers with intrinsic microporosity and thermally rearranged 66 polymers. However, the free volume in the nanoporous polymer tends to reduce 67 as a function of time which negatively impacts the gas permeance [6,7]. 68

To improve the performance of gas separation membranes, nanoporous inorganic materials (e.g., zeolites, metal-organic frameworks or MOFs, and nanoporous two-dimensional materials) have been extensively investigated [8– 11]. These materials with high porosity and thermal, chemical and mechanical robustness but mainly with pores in the range of sizes of common gas molecules can carry out molecular separations based on the relative size difference and

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adsorption affinity [12]. Besides their implementation as TFC membranes where 76 77 a thin polycrystalline film acts as a selective layer, these materials can also be used as selective fillers for a target application, constituting the so-called mixed 78 79 matrix membranes (MMMs), or when prepared as a thin film on a proper porous support, thin film nanocomposite membranes (TFN)[13]. These filler-polymer 80 combinations could overcome the main limitations of the existing membrane 81 technologies [14]: permeance-selectivity trade-off still far from commercial 82 applicability, membrane reliability and long-term realistic operation. However, 83 most of the reviews published, which timely report the current state of the art of 84 85 membranes for gas separation, lack in revealing the drawbacks and challenges in the commercialization of membranes containing nanofillers (mainly zeolites, 86 87 MOFs and 2D materials) for possible application at the industrial scale for H₂ and 88 CO₂ separation. Therefore, this review examines the contribution of nanoporous materials to constitute membranes for the separation of energy-relevant gas 89 mixtures. The main families of such materials are presented together with the 90 91 limitations and possible improvements of the current membrane systems regarding their implementation in large-scale and more practical applications. 92 Additionally, we declare the membrane requirements, membrane module 93 94 configurations and the most suggested configuration (like hollow fibers) for these gas separation applications, giving an overview of the hybrid membrane concepts 95 adapted in hollow fibers for the separation of CO₂ and H₂-containing mixtures. 96

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Fig. 1. Scheme of the different types of gas separation membranes involving
nanoporous materials. The dense or supported (also known as TFC membranes)
polymeric membranes can be MMMs (or TFN membranes) incorporating
nanoporous fillers such as MOFs, zeolites, or others.

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104 2. Zeolites and MOFs as main components of gas separation membranes

105 2.1. Opportunities of zeolites/MOFs for gas separation

Zeolites and MOFs are crystalline microporous materials, which in principle, 106 provide a straightforward strategy to overcome the trade-off limit of polymeric 107 membranes. That is, the uniform pore size offers precise molecular sieving to 108 achieve high selectivity, while the highly porous structure allows fast transport of 109 110 the smaller molecules to achieve high flux. If the pore size is adequately selected, zeolite/MOF membranes can differentiate molecules at a size difference of 0.02 111 nm or less [15]. Such clear-cut molecular sieving implies that almost every 112 important pair of the gas system can be effectively separated. 113

The pore size of zeolite/MOF membranes is mainly determined by the framework 115 116 structure. It can also be fine-tuned through ion exchange and surface modification [16]. The hybrid inorganic/organic MOF structures are much more diverse and 117 easier for surface modification. Furthermore, the permanent porosity and the rigid 118 framework structure can avoid the undesirable aging and plasticization effects 119 observed for polymers [6]. Compared to MOF membranes, zeolite membranes 120 are more stable in high temperatures, more resistant to organic solvents, and 121 more robust in harsh conditions, providing unique opportunities for system 122 integration with reactions to form innovative membrane reactors [17]. Recently, 123 significant progress has also been achieved in preparing ultrathin zeolite/MOF 124 membranes from their 2D nanosheets and further improving their membrane flux 125 [18,19]. For example, ultrathin (<50 nm) zeolite (SAPO-34) nanosheets seeding 126 layer allows the production of defect-free zeolite nanofilms (500-800 nm), which 127 displayed an exceptional orientation and facilitated transport [20]. The 128 performance was calculated as CO₂ permeance of $\approx 1.0 \times 10^{-5}$ mol (m² s Pa)⁻¹, 129 together with high CO₂/CH₄ and CO₂/N₂ selectivity of 135 and 41, respectively, in 130 equimolar binary mixtures at room temperature. Thin membranes based on 131 lamellar SAPO-34 zeolite nanosheets were also effective in separating 132 CO₂/CH₄ (selectivity=102) with a permeance of 2.5×10⁻⁶ mol (m² s Pa)⁻¹ 133 (approximately 7500 GPU) [21]. 134

Fig. 2 shows H_2/CO_2 and CO_2/N_2 separation performance from the state-of-theart zeolite/MOF membranes and their comparisons with the upper bound of polymeric membranes. As can be seen, zeolite/MOF membranes have had great success for the separation of H_2/CO_2 but much less for CO_2/N_2 when compared

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with polymer membranes. The reason is that in the H₂/CO₂ system the two transport properties that determine the membrane performance – diffusion and adsorption – often have opposite effects. That is, diffusion favours hydrogen because of its smaller kinetic size, but adsorption prefers CO₂ because of its higher quadrupole moment. Hence, to achieve a good H₂/CO₂ selectivity, the diffusion selectivity must be high. As said, zeolite/MOF membranes have a significant advantage over polymeric membranes in molecular sieving.

147 In contrast, in the system of CO₂/N₂, both diffusion and adsorption facilitate the transport of CO₂. Polymers can be easily grafted with a high density of functional 148 groups to enhance CO₂ adsorption and thus can achieve comparable 149 performance to zeolite/MOF membranes. In certain conditions when the CO2 150 affinity is strong and the temperature is low, CO2 may condense inside the pores 151 152 due to the capillary condensation effect. This blocks the transport of other gases and turns the membrane to be CO₂ selective. Most of the membranes that work 153 well for CO₂/N₂ are also suitable for CO₂/CH₄, and the selectivity is typically higher 154 155 because CH₄ has a larger molecular size than N₂ [22], e.g., face-centred cubic (fcu)-MOF/polymer hybrid membranes have exhibited exceptional separation 156 performance for energy-intensive separations considering distinct gas pairs, 157 158 including H₂/CH₄, CO₂/N₂, CO₂/CH₄ and N₂/CH₄ [23].

Despite not yet reaching the same success as for H₂/CO₂ separation, MOF membranes still hold a great potential to separate CO₂/N₂. One way is to tune the pore size to enhance the molecular sieving. In this sense, the exploration of new MOF building blocks and different topological connections should be beneficial. Another way is to improve the density of functional groups inside the MOF

channels to increase CO2 adsorption. When looking at the history of zeolite 165 166 development, most stable zeolites were discovered in the early stage. This is not surprising because zeolite synthesis is a dynamic process that tends to form the 167 most thermodynamically stable state. This trend may also apply to MOF 168 development and the MOF research community has grown to a substantial mass, 169 but most of the reported MOF systems can hardly pass the stability criteria for 170 practical applications [24]. Hence, starting from the stable MOF systems and 171 conducting surface modification should be more efficient. 172

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174 2.2. Challenges in commercialization

Membrane selectivity and permeance, membrane fabrication cost, long-term 175 stability and process reproducibility determine the commercialization potential of 176 a membrane system. The required selectivity is a process parameter that is 177 determined by the separation task. It is also the main parameter that determines 178 the process energy consumption. The higher the selectivity, the lower the energy 179 180 consumption. Membrane permeance and fabrication cost determine the capital cost. Higher membrane permeance implies less membrane area, and thus can 181 tolerate higher fabrication cost. For CO₂/N₂ separation, a selectivity of 30 and a 182 183 permeance of 1000 GPU are the estimated polymeric membrane performances to make the process economically viable [25]. The fabrication cost of MOF/zeolite 184 membranes is so far orders of magnitude higher than that of polymeric 185 186 membranes. Hence, an equivalent improvement in permeance is required to make the process competitive. The membrane lifetime is another critical factor to 187 188 determine the membrane cost. A typical lifetime is two years. The process reproducibility is a key parameter for product yield and quality control. 189

191 Factors, such as the need for robust support, lengthy and multi-step synthesis processes in batch mode, harsh synthesis conditions, such as high temperature 192 and high pressure, and special care needed to handle the brittleness, make the 193 fabrication cost of zeolite and MOF-based membranes much higher than that of 194 polymeric membranes. These challenges encourage the implementation of low-195 cost polymeric supports and the development of fast, mild, and continuous 196 fabrication processes, while the related cost disadvantage must be compensated 197 by better membrane performance. For zeolite membranes, this can be 198 compensated further by better long-term stability. For instance, high-silica 199 200 zeolites are much more stable than their low-silica counterparts. Besides the Si/Al ratio, the amount of crystal surface defects and Brønsted acid sites are also key 201 202 factors. A common approach to improve the hydrothermal stability is through surface modification using SiCl₄ or silane to eliminate the surface defects [26]. 203 Compared to zeolites, MOFs are much weaker and more sensitive to moisture. 204 205 Chemical modification to make the surface more hydrophobic is a helpful approach to improve stability [27]. However, most of the stability studies are 206 examined only in weeks' time, which is too short to be practically meaningful. 207 208 More comprehensive characterizations of the structure change (e.g., X-ray diffraction and microporosity) under relevant practical conditions in a much longer 209 210 period (> 2 months) are highly demanded.

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The process reproducibility of most zeolite and MOF membranes is still far below the satisfactory level. One of the major reasons is the presence of defects within the fabricated membranes. For zeolite membranes, most of the defects are

introduced during the thermal treatment stage, when the organic structure-215 216 directing agents are removed [28]. MOF membranes have a similar issue when the organic solvent is removed from the structure. Some innovative methods 217 using reactive agents, such as ozone, UV, and plasma, have shown good 218 potential to activate the membrane without crack formation [29]. However, how 219 to implement these approaches on large scale and at a low cost is still a big 220 challenge. Reducing the membrane thickness can help expose the structure-221 directing agents to the reactive agents and remove them with less difficulty. 222 Hence, the recent development in 2D membranes (see details in section 3)[30,31] 223 will help to improve not only the membrane permeance but also the process 224 reproducibility. Alternatively, surface coating using rubbery polymers, such as 225 PDMS, has been widely used in polymeric membranes as an effective defect 226 remedy method. it has also proved to be very helpful in MOF membranes [32]. 227 Reducing the membrane permeance, this method is a necessary step in a 228 commercial fabrication process to improve the membrane reproducibility because 229 230 of its low cost and simplicity.

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The commercialization of zeolite/MOF membranes will be also affected by the 232 233 supports' geometry as it will subsequently determine the type of membrane modules. Most of the reported zeolite/MOF membranes in the academic literature 234 are prepared on flat sheet supports because of their easy availability. However, 235 236 all the commercial zeolite membranes so far are prepared on tubular supports. Tubular supports are more robust under pressure, easy to scale up and clean, 237 238 but they are also very expensive (> 300 USD/m²) and have a low packing density (30~50 m²/m³). Compared to tubular supports, hollow fibers (HFs) share a similar 239

geometry but have a much higher packing density (see section 5), thus potentially
reducing the overall cost substantially. Hence, future studies should focus more
on how to integrate the membrane fabrication process more effectively with HF
supports.

So far, there is no zeolite/MOF membrane commercialized for gas separations, 244 but a number of zeolite membranes are on the commercialization roadmap, 245 including those with the LTA, MFI, FAU, CHA, and DDR structures [33]. The most 246 promising MOF membranes for commercialization are ZIF-8 and UiO-66 247 membranes, primarily because they are so far the most stable MOF structures 248 [34]. Moreover, ZIF-8 is made from low-cost precursors and so has a cost 249 advantage over many other MOFs. Many economical and simple membrane 250 fabrication approaches have been developed, such as counter diffusion [35] and 251 electrical field-induced growth [36-38] under the aqueous solutions. However, 252 the process reproducibility is still low and the mechanical stability under the 253 industrially relevant pressures (> 15 bar) has not been demonstrated. 254

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Some zeolite membranes, such as LTA zeolite [39], have been successfully 256 commercialized in liquid separation, which has certainly enhanced the confidence 257 258 in overcoming the abovementioned challenges in gas separation. With more industrial experiences accumulated in zeolite membranes, it is expected that the 259 production cost will be significantly reduced, and the membrane quality and 260 261 process reproducibility will be greatly improved. As the syntheses of zeolite/MOF membranes share many common features, these signs of progress will certainly 262 263 speed up the commercialization activities of the entire field in the near future.





Fig 2. Separation performances of zeolite/MOF membranes and their comparisons with the upper bound of polymer membranes. (a) For H_2/CO_2 and (b) for CO_2/N_2 . The red lines in the diagram represent the upper bound of polymeric membranes, where a membrane thickness of 100 nm is used to convert the permeance from the permeability database of polymeric gas separation membranes [40]. The data points of zeolite/MOF membranes are adapted from Ref.[41]

274 3. 2D nanoporous materials for gas separation membranes

275 3.1. Opportunities of 2D materials for gas separation

Nanoporous materials with a 2D morphology have the unique potential to constitute the thinnest selective layers ever imagined, down to the thickness of an atom, and therefore, can maximize the permselective gas flux reducing the needed membrane area and associated capital cost. Three distinct designs for selective layers can be achieved (**Fig. 3**): MMM where 2D materials constitute an ideal filler in a polymer matrix; stacked nanosheet membranes; and single-layer 2D film.

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Fig 3. Design approaches for the selective layer from 2D materials and corresponding molecular pathways. a) MMM prepared by dispersing 2D nanosheets inside a polymeric filler. b) Stacked nanosheet film by the assembly of nanosheets. c) Macroscopic single-layer 2D film.

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MMM prepared using nanoporous 2D nanosheets are extremely attractive due to 290 the high aspect ratio and nanoscale thickness of the nanosheets. This is because 291 292 a preferential orientation of the nanosheets in the matrix can be obtained, filler loading in the matrix can be maximized, and the overall film thickness can be 293 minimized. The emergence of nanoporous 2D materials with high interphase 294 compatibility with polymer (MOFs [42], g-C₃N₄ [43], covalent organic frameworks 295 [44], etc.) have led to MMM yielding improved separation performances 296 compared to the upper bound for polymeric materials. While membranes based 297

on stacked 2D nanosheet films as the selective layer offer performance
advantages over nanosheet-based MMM. The stacked nanosheet film offers a
nanoporous pathway across the entire selective layer, improving the diffusivity of
the gas molecules.

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Oriented nanosheet films can be achieved by a scalable technique such as 303 filtration on a porous support, and the film thickness can be easily regulated by 304 the amount of suspension. The separation performance from the stacked 305 nanosheet film is determined by the interplay between two transport pathways; 306 307 one constituted by the nanosheet porosity and the other by the intersheet or packing gap between the nanosheets. This gap needs to be small enough to not 308 become the primary transport pathway but also large enough so that the pore 309 openings of the nanosheets are not blocked in the turbostatically-stacked film. 310 Approaches modulating the gap, e.g., hot drop coating and reactive condensation 311 of the nanosheets have yielded promising H2/CO2 separation performance from 312 MOF nanosheets [18] and more recently from zeolite nanosheets [19]. 313 Impervious nanosheets, such as graphene oxide [45] and MXenes [46], have also 314 shown promising performance from their stacked films where gas transport takes 315 316 place through the intersheet gap. For example, graphene oxide nanosheets assembled into laminar structures have displayed fast and CO₂ selective 317 transport channels (CO₂/N₂: 91), along with exceptional operational stability [47]. 318 319 Unfortunately, the intersheet gap and the gas transport in these films are sensitive to operating conditions including feed pressure and humidity [48,49], affecting the 320 321 separation performance.

Synthesis of 2D nanosheets hosting CO2-sieving nanopores will allow the 322 323 realization of high-performance MMMs for CO₂ separation. A potential pathway 324 is the exfoliation of a suitable layered precursor, such as zeolite hosting an 8membered silicate ring. Layered SAPO-34 has been recently reported [21]. 325 Recently, synthesis of 20-nm-thick SAPO-34 nanosheets have been also 326 reported [20], Layered SAPO-34 has been recently reported [21], including its 327 exfoliation to single-layer sheets [20]. Another promising material for this is 328 ordered g-C₃N₄ such as poly(triazine imide) (PTI) which hosts 3.4 Å pores. 329 Recently, PTI nanosheets have been prepared as single-layer nanosheets [43], 330 however, the lateral size of exfoliated nanosheets was small (<50 nm), and the 331 332 yield of exfoliated nanosheets was low. Synthesis of high-aspect-ratio g-C₃N₄ nanosheets with high yield would be highly beneficial in this respect. 333

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Macroscopically-large 2D films, such as graphene and analogues, can be used 335 to fabricate membranes with a selective layer that is just one atom thick. When a 336 high density of gas-sieving pores is incorporated in graphene, extremely large 337 permselective gas flux can be realized [50]. Molecular simulations predict 338 permselective CO₂ permeance in the range of 10000-100000 GPU [51]. A CO₂ 339 340 permeance of 10000 GPU has been recently demonstrated in combination with an attractive CO_2/N_2 selectivity (>20)[51,52]. This is mainly because of the 341 extremely short diffusion path length of gases across the atom-thick pores of 342 343 graphene [53]. Gas sieving can be obtained from nanopores hosting electron density gap comparable to that of the target gas molecules. For such nanopores, 344 the flux of gas molecules can be modelled using the transition state theory and is 345 determined by the energy barrier experienced by the molecule while crossing the 346

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nanopore [54]. As a result, the relative size of the gas molecules with respect tothe nanopore determines the gas pair selectivity.

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There are three key challenges in developing size-sieving nanoporous graphene 350 membranes: angstrom-scale pores have to be created with dimensions able to 351 sieve the desired components (e.g., CO₂ or H₂); pore creation technique has to 352 be precise to yield a narrow pore size distribution avoiding large nonselective 353 pores; and the density of gas-permeable pores should be high enough (>0.1%) 354 to outperform the conventional membranes. Meeting these requirements would 355 realize membranes, which are highly permeable but also selective, overcoming 356 the selectivity-permeability trade-off of conventional polymeric membranes. This 357 will require the development of synthetic approaches where pore nucleation and 358 359 expansion can be controlled, e.g., down to the removal of 10-16 carbon atoms per pore in the case of graphene for H_2 - and CO_2 -sieving [52]. 360

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The control of pore density (nucleation) and size (expansion), permitting 362 maximization of gas flux and gas pair selectivity, will be highly beneficial. For 363 CO₂/N₂ separation, exploiting the higher adsorption affinity of CO₂ by 364 365 functionalizing with CO₂-philic groups is an attractive approach [55,56]. Although the field is in its infancy, attractive separation performance has been 366 demonstrated for applications where large permeance is desired along with a 367 368 moderate selectivity, e.g., post-combustion carbon capture. For instance, nanoporous graphene membranes prepared by controlled pore formation and/or 369 370 functionalization have yielded CO₂ permeances of 10000 GPU along with an attractive CO₂/N₂ selectivity (above 20)[57]. Advances on the fundamental fronts 371

- especially mechanistic understanding of nanopore formation - are expected to
 further improve the separation performance toward improving the gas pair
 selectivity.

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376 3.2. Challenges in commercialization

A challenge for MMM and stacked nanosheet films is to develop strategies to 377 reduce their thickness down to that of the selective layer in TFC (<100 nm). For 378 this, the development of low-cost, smooth, and porous polymeric support hosting 379 asymmetric porous structure with nanometer-scale pore opening will be highly 380 attractive. Such a support structure would allow the formation of a uniform thin 381 film while avoiding pinhole defects. Nonsolvent-induced phase separation of 382 polymer is a promising technique to produce such porous supports. In cases 383 384 where high thermal stability is required, high-glass-temperature polymers, such as polybenzimidazole [58], are attractive. 385

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387 In the case of single-layer 2D films such as nanoporous graphene film, a key challenge lies in developing synthetic methods that are conducive to scale-up. 388 Large-area polycrystalline graphene films can be synthesized on a metal foil by 389 390 chemical vapor deposition (CVD), a scalable method that can produce hundreds of meter squares of graphene, e.g., by a continuous roll-to-roll process [59] or by 391 stacking the metal foil [60]. However, the CVD technique has to be optimized to 392 393 yield graphene at a large scale with high enough quality for membranes, i.e., with an extremely low density of defects and contaminations. The cost of catalytic 394 395 metal foil used for CVD of graphene needs to be reduced to or lower than 10 \$/m². Alternatively, methodologies allowing the reuse of the foil for several rounds
of synthesis can cut down the effective cost of foil.

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For nanoporous single-layer graphene membrane, another critical challenge is 399 the scalable incorporation of nanopores into an otherwise impermeable graphitic 400 lattice. Direct synthesis of nanoporous graphene is highly attractive in this regard 401 (top-down approach). Proof-of-concept for this has been demonstrated by 402 lowering the CVD temperature [61,62] or by controlling the amount of carbon 403 precursors for the synthesis of graphene [63]. For pore incorporation by post-404 synthetic etching (bottom-up approach), scalable chemical etching techniques 405 involving gaseous etchants are highly attractive. Reactive gases can be exposed 406 uniformly over the surface of graphene in simple setups. However, controlling 407 408 pore nucleation and expansion at the Å-scale in an industrial-sized reactor is expected to be challenging for both top-down and bottom-up approaches. An 409 improved mechanistic understanding of events, which control pore-size 410 distribution, is needed to achieve a high pore density with a narrow size 411 distribution. 412

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From a membrane fabrication perspective, a crucial challenge is to develop methods for transferring the graphene film onto a porous support without inducing cracks or tears in the film. CVD graphene is synthesized on a substrate, and the transfer of graphene involves its isolation from the growth substrate. The mechanical stress generated during the isolation step is often high enough to generate macroscopic cracks in graphene, which deteriorates gas pair selectivity. Recently, crack-free centimeter-scale graphene membranes have been demonstrated by permanently reinforcing graphene with a gas-permeable layer, such as nanoporous carbon film [64], carbon nanotube film [65] and dense polymer films [52]. However, these methods require further improvement for the preparation of graphene membranes on low-cost and flexible support, such as those used for the preparation of polymeric TFC membranes.

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427 4. Current technical limitations of asymmetric membranes presenting a

428 selective layer with nanoporous materials

429 4.1. Asymmetric membranes for gas separation

In general, dense and thick polymeric membranes with no porous structure are 430 mostly applied for characterization purposes or to test new membrane materials. 431 Their single-gas permeability and ideal selectivity for a given mixture can be 432 obtained with the so-called time lag system with the advantage of allowing the 433 estimation of diffusivity and solubility parameters of the membrane [66]. However, 434 this experimental setup is not very realistic, as in real-world applications mixtures 435 of gases are used, including minor components such as moisture or H₂S, 436 depending on the origin of the stream to be treated. 437

Instead, asymmetric membranes with a selective skin layer on top of a mechanically stable support constitute the perfect membrane structure, and one which could be ideal for commercial applications. The advantage of asymmetric membranes is that transport resistance is minimised and fabrication costs are reduced by using the minimum amount of selective material. This type of membrane supposes two in-series resistances to the gas transport and the contribution of the support has to be minimum so as not to penalize the function of the selective film [67]. As a consequence, the porosity of the support has to be
as high as possible while providing an adequate activated surface to favour the
deposition of the ultrathin film by certain coating techniques [2].

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Sometimes an intermediate gutter layer is placed between the previous two 450 layers. A gutter layer is an intermediate layer between the top selective layer and 451 the surface of the membrane support. The gutter layer can modify the surface 452 defects, plug the pores of membrane substrate and prevent the selective coating 453 dispersion from penetrating deeply into the pores. It also provides a smooth 454 surface bed for the top selective layer so that it is easier to spread a thinner layer 455 than to coat directly on the relatively rough substrate. As a result, the gutter layer, 456 even if it contributes to the whole transport resistance, can enhance the overall 457 permeance of the membrane by an order of magnitude [68], having found that 458 the gutter layer permeability should be 5-10 times higher than that of the selective 459 layer to minimize the decrease in selectivity [69]. 460

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462 *4.2. Limitation of support*

In addition to conferring mechanical stability to the membrane, the support, in series with the skin layer, should minimally restrict the membrane transport. As an example, PEBA (poly (ether-block-amide)) type polymers, commercialized as Pebax[®], are some of the most studied skin layers for CO₂ selective membranes.

Fig. 4 illustrates the expected effect of the membrane thickness on the
 permeance for elastomeric Pebax[®] 1657 membranes. From nine relevant
 studies, an average CO₂ permeability of 101±34 Barrer was obtained for Pebax[®]

1657 thick dense membranes (corresponding to CO₂/N₂ selectivities in the 36-89 471 472 range) [67,70-77]. The dotted line of negative slope is the calculation of permeance as a function of skin layer thickness from the value of 101 Barrer 473 (dividing permeability by membrane thickness), implying negligible resistances 474 from the support and gutter layer. Even if gas separation supports are highly 475 permeable (ca. 200,000 GPU of CO₂) [78,79], in practice, the TFC membranes 476 of only Pebax® 1657 (red squares) exhibit lower permeances than expected due 477 to the negative contributions of both the support and the gutter layer. The 478 deviation augments with decreasing selective layer thickness. The blue triangles 479 480 in the plot correspond to Pebax® 1657 based MMMs, always with permeances above the expected, in line with the capacity of fillers to enhance the permeation 481 of such membranes [80]. From this plot, we can conclude that as the skin layer 482 483 thickness goes down to the nanometer dimension, the resistance of the support becomes more relevant suggesting its improvement in terms of porosity, 484 thickness and mechanical strength. Moreover, MMMs can enhance the 485 permeance beyond the thickness-related value. 486



Fig. 4. CO₂ permeance as a function of the thickness of the Pebax® 1657 488 489 selective layer for different TFC membranes. The dotted line was obtained from the average of the permeabilities of nine different dense membranes [67,70-77]. 490 The red squares and blue triangles correspond, respectively, to bare polymer 491 [67,81-85] and to filler modified [69,85-87] TFC membranes of different 492 thicknesses. These membranes are known as TFN membranes, i.e. TFC 493 membranes incorporating porous particles. When the membrane thickness is 1 494 μ m, a permeance of 1 GPU (1 GPU= 1.10⁻⁶ cm³(STP).cm⁻².cmHg⁻¹.s⁻¹) 495 corresponds to a permeability of 1 Barrer. 496

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498 4.3. Further developments in gutter layer and support

The highest permeance gas separation membrane ever reported, with 40,000 499 GPU of CO2 and 10-12 CO2/N2 selectivity, was made of PDMS [79]. This 500 501 membrane was 34 nm thick and prepared onto a glass substrate by spin coating, which was later detached using ethanol and thus transferred onto highly 502 permeable PAN (polyacrylonitrile) ultrafiltration support; in this way, it was 503 504 avoided the use of a gutter layer and the possible penetration of the PDMS within the substrate pores. Indeed, to extract the maximum performance of the selective 505 layer, the resistances of the gutter layer and support have to be as negligible as 506 507 possible.

508

The typical approach is to fill the support porosity with some liquid to avoid the penetration of the gutter material [78,88], but there are other interesting approaches such as the use of sacrificial gutter layers [67,89]. In this case, the sacrificial material should be removed without altering either the membrane

separation properties or its attachment to the support. The PDMS membrane 513 514 mentioned previously with the 40,000 GPU CO₂ permeance was first prepared by spin coating on a sacrifice layer of poly(4-hydroxystyrene)[79]. This was 515 dissolved in ethanol and then the PDMS transferred to a PAN support maintaining 516 its shape and mechanical strength. Even if it is true that the extrapolation of this 517 methodology to a scalable industrial procedure and with more selective polymers 518 than PDMS (this is more a gutter layer material than a desirable selective 519 polymer, at least for CO₂ separation) may not be immediate, these results are 520 quite encouraging. In fact, with this principle, a 70 nm thick polyetheramine-521 graphene oxide Pebax 1657 membrane has been prepared on a 75 nm thick 522 PDMS gutter layer showing a CO₂ permeance of 1455 GPU together with a 523 CO₂/N₂ selectivity of 68.1 [69]. In addition, one of the most promising membranes 524 for CO₂ separation is the Polaris[™] one, made of a proprietary polymer presenting 525 a gutter layer strategy and commercialized by Membrane Technology and 526 Research, Inc., with up to 2000 GPU of CO2 and CO2/N2 selectivity of 50 [90,91]. 527 528

529 **5. Membrane configurations and process requirements**

To further improve the separation properties of thin layers, several microporous 530 531 materials (like MOF) with exceptional molecular sieving ability are being filled in a composite (or MMM) layer onto HFs (see Fig. 5). However, a non-compelling 532 physical and chemical compatibility among inorganic and organic phases in 533 534 composites may compromise the result of enhanced separation performance. In the future, particular emphasis should be placed on the resulting structural 535 536 changes to the membrane formulation when extrapolated from flat to HF 537 configuration.



Asymmetric structure

540

Fig. 5. Composite hollow fibre membranes for gas separation. Cross-section view 541 of polybenzimidazole-10 wt.% ZIF-8 mixed matrix asymmetric hollow fibre for 542 H₂/CO₂ separation [92]. 543

544

Asymmetric membranes can be manufactured in a flat or a HF geometry and then 545 packed into modules to reach high productivity for industrial applications. Fig. 6 546 graphically illustrates the types of membrane module configurations, which 547 548 typically refer to the geometry of the membrane and its position in space in relation to the flow of the feed fluid and of the permeate. HF [93] and spiral wound 549 [87] are the membrane configurations providing the highest values of 550 intensification in terms of membrane area per module volume (i.e., packing 551

density). HF modules stand out as the most preferred due to their high packing density, varying from 500 up to 9000 m² m⁻³, exceeding the reported densities for spiral-wound modules (ca. 1200 m² m⁻³) and plate and frame modules (ca. 100– 400 m² m⁻³) [94]. HF membranes also have the benefit of being able to handle extremely high transmembrane pressure difference (approximately 70 bar), while the fabrication cost is around 5–20 times lower than the equivalent for spiral wound modules [95].



560 **Fig. 6**. Graphical depiction of the four types of membrane configurations.

561

559

Most commercially available membranes are manufactured as HF modules, while 562 less than 20% correspond to spiral wound modules. Both are most suitable for 563 564 gas separation applications [96], as they are relatively less prone to membrane fouling than flat sheet or tubular modules. In general, HF modules experience 565 25% more membrane surface shears promoting hydrodynamic pattern changes 566 which consequently mitigate the deposition of foulants, e.g., when operating HF 567 modules in cross-flow filtration mode, shear forces on the membrane occur 568 thanks to bubbling, vibration, or particle scouring [97]. However, in the case of 569

HF modules, the feed gas requires further pre-treatment to mitigate severe fouling and plasticization, depending on the type of material. As for spiral wound modules, apart from being more resistant to plasticization, can be applied to a wider range of membrane materials compared with HFs [95]. To date, few spiral wound membranes for gas separation (at least for CO₂ and H₂-containing mixtures) have been documented [98–100].

576

Today, the production of HFs with a selective layer is still challenging for gas separation since gas molecules are sized in the Angstroms range [101], and are therefore very sensitive to any defect in the functional layer. The usage of an atomically thin layer with precisely controlled pores and chemical functionality is crucially needed to achieve true molecular sieving of gas molecules [102], as this separation mechanism is usually compromised by surface adsorption and condensation phenomena of the gas molecules in the membrane pores [103].

584

585 Forming ultrathin membranes into HF modules is an ongoing research challenge, but they still represent a promising way for efficient gas separation with scalable 586 productivity and less economic expenditure [96]. Various ultrathin composite HF 587 588 membranes for CO₂/H₂ separation have been successfully synthesized at lab scale (Table 1). MOFs (such as ZIF-8, Cu₃(BTC)₂, MIL-53 and UiO-66-NH₂) are the 589 most reported nanoporous fillers in composite HF fabrication due to their physical 590 591 and chemical compatibility with polymer phases; however, such membrane modules are limited to small membrane sizes of 10-48 cm length. 592

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Composition	Type of HF		Membrane/module	Gas	Operating	Permeance in GPU	Selectivity	Reference
			size	mixture	conditions	(of faster gas)		
ZIF-8/Ultem®	Mixed matrix		6 fibers/ 20 cm length	CO_2/N_2	45∘C, 6.8 bar	34	28	[104]
			each					
PTPESU	Asymmetric		10 fibers/ 15 cm length	CO_2/N_2	25 ∘C, 3.5 bar	85.1	34	[105]
			each					
PBI/P84	Asymmetric		1 fiber/ 17 cm length	H ₂ /CO ₂	180 °C, 6 bar	90	13.5	[106]
Pebax/PDMS/PAN	Composite		1 fiber/ 15-20 cm length	H ₂ /CO ₂	25 °C, 2 bar	59.8	8.1	[107]
PVA/PPO	Thin	film	10 fibers/ 10 cm length	CO ₂ /N ₂	25 °C, 2 bar	791	40	[108]
	composite		each					
PDMS/PAN	Thin	film	1 fiber/ 15 cm length	CO ₂ /N ₂	25 °C, 3 bar	5000	11	[109]
	composite							
sPPSU/PBI	Dual-layer		1 fiber/ 15 cm length	H ₂ /CO ₂	90 °C, 14.2 bar	16.7	9.7	[110]
TNTs/PSf	Mixed mat	ix	10 fibers/ 20 cm length	CO ₂ /N ₂	25 °C, 3 bar	120	28.8	[111]
			each					
ZIF-8/PBI	Mixed mat	ix	1-22 fibers/ 18 cm	H ₂ /CO ₂	150 °C, 7 bar	107	18	[92]
			length each					

 Table 1. Various hollow fibre (HF) membrane concepts aimed at separating CO2 and H2 containing mixtures.

71E-8/Si-N/	Ceramic	1 fiber/ 10 cm length	Ha/COa	25 °C 2 5 bar	2505	11 7	[112]
217-0/31314	Ceramic		112/002	25 C, 2.5 Dai	2000	11.7	[112]
PDMS-	Asymmetric	1 fiber/ 15 cm length	CO_2/N_2	25 °C, 5 bar	109	31	[113]
Cu ₃ (BTC) ₂ /PSf							
PEI/Aminosilane	Mixed matrix	10 fibers/ 48 cm length	CO_2/N_2	35 °C, 5 bar	30.9	34.7	[114]
functionalized		each					
MIL-53							
PIM/PDMS/PAN	Asymmetric	3 fibers/ 16 cm length	CO_2/N_2	25 °C, 2 bar	483	22.5	[115]
	composite	each					
Pebax® 2533-UiO-	Mixed matrix	1 fiber/ 7-10 cm length	CO_2/N_2	25 °C, 2 bar	26	37	[116]
66-NH₂/PP							
Abbreviations: PTPES	U (poly trimethyl p	henylene ethersulfone); PE	I (polybenz	imidazole); sPPSU	(sulfonated poly	phenylsulfone); PV	A (poly (vinyl alcoh

PDMS (polydimethylsiloxane); PAN (polyacrylonitrile); PPO (poly(p-phenylene oxide)); TNT (titania nanotube); PSf (polysulfone); PEI (polyetherimide); PIM

(polymer of intrinsic microporosity); PEI (polyetherimide), PP (polypropylene).

Depending on the type of polymer (or dope solution composition) and preparation 599 600 protocol, polymer composite HFs can display high permeation rates in gas separation performance. This is the case of PDMS/PAN thin composite, which 601 has shown up to 5000 GPU permeance in CO₂/N₂ mixtures [109], while 602 603 PIM/PDMS/PAN HFs displayed 483 GPU (with selectivity values of 22.5) towards similar gas mixture [115]. In this HF, a cross-linked PDMS gutter layer was 604 introduced between the PIM selective layer and the PAN substrate, which was 605 able to mitigate the detrimental solvent effects during the dip coating, permit PIM 606 to adhere to it, and redistribute the gas transport across the membranes. 607

608

Compared with such HFs, PDMS-Cu₃(BTC)₂/PSf [113] and PEI/aminosilane 609 functionalized MIL-53 [114] HFs offered better performance with CO2/N2 610 611 selectivities of 31 and 34.7, respectively, but with a decreased CO_2 permeance. ZIF-8 filled polyetherimide (Ultem® 1000) matrix was subsequently utilized for the 612 fabrication of dual-layer asymmetric HF membranes via the dry jet-wet quench 613 method [104]. The resulting MMM HFs showed a 20% increased permeance in 614 CO₂/N₂ testing compared with the pristine HFs. In this regard, these few 615 examples evidence that the involvement of inorganic materials, like MOFs, with 616 617 superior gas molecular sieving nature, can enhance the CO₂/N₂ separation performance of polymer membranes [18]. Similarly, specific MOFs can be 618 adapted in HFs presenting polymer or inorganic membrane supports for H₂/CO₂ 619 620 mixture separation. For instance, ZIF-8 has contributed to a 65% increase in H₂ permeance at constant ideal selectivity in PBI HFs. Unlike pristine PBI HFs, filler 621 622 incorporation into the PBI matrix contributed to a substantial increase in H₂ permeance from 65 GPU to 107 GPU, while the ideal H₂/CO₂ selectivity remained 623

unchanged (ca. 18)[92]. Knowing the great advantages of ceramic materials in terms of high thermal and chemical stability in harsh environments, they have started to be applied as HF supports. As an example, ZIF-8 supported on silicon nitride ceramic HF exhibited improved permeation as high as 2,505 GPU, with H₂/CO₂ selectivity of 7.3 [112].

To date, most advances in composite polymer-based membranes containing 629 630 either MOFs or zeolites have relied on the fabrication of flat sheet membranes, 631 which have exhibited impressive performance surpassing polymer upper bound performance, e.g., MMMs based on ZIF-300 filled PEBA [117]. This is a result of 632 engineered designs of the polymer and inorganic phases. Unfortunately, there is 633 still limited research on HF membranes but studies show that they represent the 634 most prominent membrane configuration for separating CO₂ and H₂-containing 635 636 mixtures (see Table 1), at least in H₂/CO₂ and CO₂/N₂ mixture separations with scalable performances for possible industrial purposes [96]. Certainly, several 637 factors should be considered when tailoring a HF membrane, such as inorganic 638 639 and organic (i.e., polymer) phase properties, along with their compatibility with each other. 640

To some extent, the dope solution composition has a fundamental and decisive 641 642 impact on the morphology and structure of prepared membranes and thus on gas separation performance. Therefore, particular emphasis must be placed on the 643 fabrication parameters[118]; for instance, the dry-jet wet spinning process stands 644 out as the most used method for HF preparation, where several variables, such 645 as bore fluid composition, flow rates of dope and bore fluids, and air gap, are 646 essential to obtain defect-free membranes. However, as for the selection of 647 648 membrane material (both the support and the selective layer), the presence of humidity and impurities (e.g., H₂S)[88], as well as operating temperature and
pressure, are also important for targeted separations.

651

Since most industrial separations demand large membrane areas (ca. 1000 -652 millions m²), the major challenge impeding the industrialization of new membrane 653 654 materials in HF configurations lies in producing membranes in a large quantity with high permeance and selectivity at a reasonable cost [119]. Table 1 reports 655 successful examples of new composite membranes in small HF modules; 656 however, there is no report in which any of those membranes have been 657 658 extrapolated to a large scale. Developing scalable methods to obtain reproducible permeance and selectivity in large HFs thus still remains highly challenging. 659

660

661 6. Conclusions and outlook

Current and future energy production processes involve the separation of CO2 662 and H₂-containing mixtures. In this context, membrane technology seems to be 663 the most suitable approach from the point of view of process simplicity, cost and 664 665 sustainability. Besides, membranes based on or modified with nanoporous materials have demonstrated very good performance when separating CO₂/N₂, 666 667 CO₂/CH₄ and H₂/CO₂ energy-related mixtures. Nevertheless, some limitations still remain to achieving the industrialization of membranes in this field, even if 668 selectivity-permeance upper bounds have been surpassed with the help of many 669 670 nanoporous materials.

671

For 2D materials, such as nanoporous graphene, control of pore size and porosity can still be enhanced by an improved mechanistic understanding of pore incorporation. The thickness decrease in the selective membrane skin layer
would overcome issues like membrane activation and even the cost of relatively
expensive nanoporous materials. However, large-scale, effective methods for
transferring 2D films to porous supports without incurring defect formation are
needed.

The ability to implement flat membrane procedures to process intensified spiral wound and HF membrane systems has to be improved. Moreover, some issues like support adequacy in terms of mechanical and diffusion resistances (requiring or not of a gutter layer), fabrication reproducibility and cost, mechanical robustness and long-term stability need attention to achieve commercially reliable membrane systems.

All these limitations suggest the concentration of efforts in two directions: more interdisciplinary work is needed combining chemistry, materials science and chemical engineering to extract the best of nanoporous materials when allied with the other membrane components; and more academic-industry collaboration is desired focussing on specific energy-relevant gas mixtures to be separated under realistic conditions.

691

692 Recommendations for the researchers in the field

For a possible real application, the gas mixtures must present contaminants (e.g., H₂S, CO), water and other gases, which strongly affect the membrane performance [120]; e.g., CO₂ and N₂ permeability can decrease as water occupies free volume in polymer membranes, while the N₂ permeability could increase in the presence of H₂S by improving the N₂ solubility or diffusion within specific polymers (e.g., PDMS) [120]. To date, most of the research has been done at a lab-scale, therefore, there is a need of extrapolating the performance to a larger scale (e.g., pilot scale), this is related to finding scalable fabrication methods with reproducibility in membrane performance. This may also imply the handling of operating conditions for better performance. For example, as for CO₂ separations, feed CO₂ concentration influence the separation performance (particularly gas flux) since there is different CO₂ partial pressure across the membrane.

In addition to this, when testing under zero transmembrane pressure using sweep gas, the non-selective viscous flow is minimized through the membrane defects resulting in enhanced selectivity. In realistic practical conditions, a non-zero downstream pressure exists, leading to higher solute concentrations in the membrane. This aspect should be also considered when testing the membrane performance.

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