



Regular Article

A Review on the Effects of Fillers on the Gas Separation by Mixed Matrix Membranes

H. Asadi¹, O. Alizadeh^{1*}, A. Ramazani^{2,3}, F. Dorosti¹

¹ Department of Chemistry and Chemical Engineering, Rasht Branch, Islamic Azad University, Rasht, Iran

² Department of Chemistry, Faculty of Science, University of Zanjan, P. O. Box: 45195-313, Zanjan, Iran

³ Research Institute of Modern Biological Techniques (RIMBT), University of Zanjan, P. O. Box: 1045195-313, Zanjan, Iran

ARTICLE INFO

Article history:

Received: 2022-08-13

Accepted: 2022-10-30

Available online: 2022-10-30

Keywords:

Metal-Organic Framework,
Mixed Matrix Membranes,
Gas Separation

ABSTRACT

The Mixed Matrix Membrane (MMM) concept consists of incorporating inorganic or organic fillers in suitable polymers. The majority of polymeric membranes maintain a trade-off between permeation and selectivity, which restricts their development in separation applications. In this paper, less reviewed challenges on the development of MMMs, such as the preparation of mix-matrix resistant membranes for industrial gas separation applications, as well as the use of appropriate and compatible fillers for different types of polymers were discussed. MMMs comprising Metal Organic Framework (MOF) fillers were extensively studied. The importance of MOFs includes the finely tunable structures, excellent compatibility with polymer matrices, and molecular sieve actions. MMMs are considered promising structures that combine the advantages of polymeric and inorganic membranes. They exhibit the potential to upgrade the separation performance of pure polymer membranes using filler materials, whereas the cost remains relatively lower than that of pure inorganic membranes. The development of novel filler materials makes a substantial contribution in terms of role-playing.

DOI: 10.22034/ijche.2022.355949.1454 URL: http://www.ijche.com/article_159697.html

1. Introduction

The membrane separation leads to the energy efficiency and cost-effectiveness in many gas separation applications [1]. The unique properties that membranes can offer have led

to an increase in the use of these systems in industry [2]. Among the separation methods, membranes are easy to install and require minimal supervision [3]. Additionally, membranes have no moving parts, demanding

*Corresponding author: alizadeh@iaurasht.ac.ir (O. Alizadeh)

smaller spaces, and less maintenance [4]. Furthermore, they represent an environmentally friendly technology as they require only a small amount of energy to operate and do not allow gas emission or mixing with solvents [5]. Additionally, membranes can be conveniently scaled, facilitating commercialization [6]. The gas separation through membranes has seen a ceaseless growth in the recent past because of its low-carbon footprint, high-efficacy and modest energy requirements [7-11]. Membranes can function in an uninterrupted way with minimal maintenance and they can selectively transport species depending on their permeability that is to say membranes can resemble a molecular filter that organizes components via aiding some molecules to permeate in a selective manner while hindering their counterparts in terms of size and other physical properties. This subject has swiftly expanded in gas separation applications by advanced synthetic membranes, which can be large in scale and significantly efficient in energy [10]. Membranes continue to be alluringly applicable to the majority of gas separation industries, e.g., the landfill gas recovery, natural gas processing, air separation, Olefin/paraffin separation, hydrogen recovery, etc. [12-15]. However, due to the economic competitiveness in the separation technologies and the current challenges and difficulties associated with aggressive environments for membranes, many applications are in need of highly robust and effective membrane materials featuring greater selectivity and permeability. The issue of membrane materials development should be considered to synthesize both higher performance and more durable membranes [16, 17].

Following the quick progress of researches

within the last forty years, membrane technologies have significantly been applied in industries such as the wastewater treatment [18], desalination [19], organic solvent dehydration [20], and gas separation (CO₂ removal, H₂ isolation, O₂ enrichment) [21]. Upon investigating gas diffusion through the PDMS membrane in 1968, Robb began the removal of carbon dioxide [22]. Later in 1989, the above research work was enhanced by Stern, who found the gas permeability coefficient at higher temperatures [23]. Air Products and Chemicals Inc. (1980) developed the first large-scale membrane with the goal of the hydrogen separation from methane. In their design, the hollow fiber membrane composed of Polysulfone was employed [25, 26]. Later (1983), Separex and Cynara manufactured a cellulose acetate membrane for the same application [26]. In future years, nitrogen derived from air via membranes was presented [27]. Hereafter, membrane systems were developed to deal with hydrogen sulfide removal from methane, oxygen enrichment, air dehydration, and volatile organic compounds (VOCs) removal from air [3]. Some of the most important industrial examples of membrane applications in the gas separation industry are listed in Table 1 [28-30].

Researches on MMMs comprising polymeric materials and inorganic components [31-44] began following the introduction of this basic idea more than 30 years ago by Kulprathipanja et al. [45]. Chung et al. [46] carried out a progression review on this topic. There remain a number of challenges, including chain rigidification pore blockage, and interface voids [32, 33, 46]. Moreover, existing troublesome issues, including the oversize of zeolite nanoparticles and the poor interface between the polymer matrix and their mutual agglomeration, need to be resolved

prior to applying commercialization. One approach to overcoming these challenges is to determine novel selective fillers that are characterized by inborn nano size, minor aggregation, and more efficient interactions with the polymer matrix. So far, little research has been done on reviewing the use of mixed matrix membranes and the effects of

membrane fillers for gas separation applications.

This study provides an extensive review on the applications of polymers in the gas separation industry and discusses the types and impacts of fillers, employed to enhance MMMs separation capabilities.

Table 1

Industrial examples of membrane application in the gas separation.

Process	Components	Reference
Purification of natural gas	H ₂ S/CH ₄	[28]
	CO ₂ /CH ₄	
	H ₂ O/CH ₄	
	C ³⁺ /CH ₄	
Hydrocracker	H ₂ /light hydrocarbons	[28]
Hydrotreatment	H ₂ /H ₂ S	[28]
Steam-methane reforming	H ₂ /CO	[29]
Ammonia plant	H ₂ /N ₂	[30]
Polyolefin plant	VOCs/N ₂	[30]
Refinery waste gases	VOCs/Air	[30]
	H ₂ from other gases	
	CH ₄ from other gases	
	CO ₂ from other gases	

2. Membranes principles

Based on the International Union of Pure and Applied Chemistry (IUPAC), a membrane represents a form of structure of which lateral area is greater than the thickness by which transfer may take place considering the role of driving forces [47]. This description appears identical to the meaning of the thin film; however, IUPAC describes a thin film as a film of which thickness is of the order of a characteristic scale or smaller [48]. A membrane and a thin film are different in that; the former is thin-structured like a film (no solid necessarily) that detaches fluids (gases, vapors, or liquids), thus acting as a selective obstacle and helping special substances to

move through, while preserving others. However, given their mechanical properties, thin films are attached to a layer and do not play the same role necessarily, thus are part of the membrane similar to those of the Thin Film Composite (TFC).

The membrane technologies are swift separation technologies, which are quite modern and therefore might be employed in environmental remediation, pharmaceutical, chemical, green energy, and food sectors [43-54]. In most respects, six main membrane processes have been found useful in such applications as ultrafiltration (UF), microfiltration (MF), electrodialysis (ED), the gas separation (GS), reverse osmosis (RO) and

pervaporation (PV).

The membranes are categorized as metallic, inorganic, and polymeric in terms of material [55]. The metallic membranes composed of palladium (Pd) or platinum (Pt) enjoy quite a performance; however, the price of valuable metals significantly affects the choice of membranes. Inorganic membranes represent a viable substitute for the metallic ones due to their better chemical stability and lower costs of establishment [56]. Currently, polymeric membranes are frequently used throughout the industry due to their competitive performance and being outstandingly economical [57]. The membranes are able to function at ambient temperature and have desired chemical and mechanical properties [58]. However, high temperatures ranging from 200 to 900 °C are required for inorganic membranes to function. Given the cost-effectiveness and less energy requirements of polymeric membranes, they exhibit high potential for being used in industry-scale gas-separation processes, including carbon dioxide capture, nitrogen purging (O₂/N₂), hydrogen recovery (H₂/N₂, H₂/CH₄), natural gas sweetening (H₂/CO₂, CO₂/N₂, CO₂/CH₄), etc. [24, 59-62].

The morphology of membranes (chemical and physical structures), nature of penetrating species (shape, size, and polarity), and interaction membrane-permeable species justify the membrane-wise gas permeability [63-65]. Initial membrane characteristics and the nature of penetrating species constitute the divisional features of a particular gas through membrane. The membrane-permeability interaction as the third property contributes to the gas solubility or sorptivity in the membrane. The permeability PA of a permeant "A" results from the solubility (thermodynamic parameter), SA, and diffusion coefficients (kinetic parameter), DA [66].

$$PA = SA \cdot DA \quad (1)$$

Membrane permeability, PA, can be determined based on the measured parameters as follows:

$$PA = \frac{Q_A \cdot L}{\Delta P \cdot A} \quad (2)$$

Herein, Q_A is the volumetric flow rate of the gas 'A' subjected to normal temperature and pressure, ΔP is the trans-membrane pressure decline, L is the efficient thickness of the membrane, and A the membrane surface area. Permeabilities are commonly presented in Barrers, in which 1 Barrer is equal to 1 × 10⁻¹⁰ (cm³ STP. cm cm⁻² cmHg⁻¹ s⁻¹).

Selectivity is the ratio of the single-gas permeability from a mixture of species permeating through the membrane. Selectivity (or permselectivity) indicates the permeability of penetrant 'A' divided by that of the second permeant 'B':

$$\alpha_{AB} = \frac{P_A}{P_B} \quad (3)$$

The gas transport separations in membranes is executed through the absorption, diffusion, and desorption of molecules on membranes, and depends on driving forces such as pressure (ΔP), temperature (ΔT), gradient concentration (ΔC), and electric potential (ΔV).

3. Polymeric membranes

Polymeric membranes convert into prevalent practical materials needed for many applications of the gas separation including the petroleum refinery [68], landfill gas recovery [69], natural gas sweetening [67], flue gas separation and hydrogen recovery and purification [70]. This might be due to their mechanical strength, processability, scalability and economic competitiveness [71-72]. Anyway, polymeric membranes remain

vulnerable to a balance between the gas selectivity and permeability in terms of Robeson's upper-bound. Inorganic materials are combined into polymeric membranes to circumvent the mentioned restriction.

After fabricating a membrane composed of cellulose acetate used in the desalination of water via reverse osmosis, Sourirajan and Loeb initiated the transformation of polymeric membranes in the 1960s [73]. A porous substrate carried a 0.2 μm thin membrane and it was able to convert seawater into potable water. Moreover, they determined the applicability of cellulose acetate membrane for the gas separation [74-76].

Polymers are divided into two categories according to their structural characteristics. Unlike glassy polymers, rubbery polymers can go back to their original shape once stretched [77]. In addition, rubbery polymers appear to be having greater permeation and lower selectivity since the mechanism of transport is managed through absorption instead of diffusing [78]. In return, glassy membranes are of greater selectivity and lower permeation given their limited diffusion. This shows that the tradeoff between selectivity and permeability makes it hard to have a polymer with both of the specifications.

Polymeric membranes of the glass type dominate industrial membrane separations due to the favorable mechanical properties and high gas selectivities. The number of rubbery polymers employed in the gas separation is a few compared to that of glassy polymers, especially poly dimethylsiloxane (PDMS). Glassy polymers including polyamides, polyimides, polyarylates, Polysulfone, polycarbonates, polyacetylenes, cellulose acetate, poly (phenylene oxide), cardo-type polymers, and poly [1-(trimethylsilyl) -1-propyne] (PTMSP) are widely investigated as

polymeric materials in the gas separation [79]. Polyethersulfone and Polyimide are the highly studied polymer components for membranes, given that each displays higher gas permeability and greater gas selectivity than the majority of other glassy polymers. They enjoy desired mechanical properties as well as higher thermal and chemical stability in the achieved membranes.

Structural adaptations are needed to improve the permeation properties of polyimides [63-80]. In many cases using gas, usually, polymeric membranes comprise dense thin layers [81]. To ensure that mechanical properties are improved, the dense layer is placed on a substrate with many pores [82]. The theory based on the solution diffusion model is accepted for the transport mechanism [83]. This model composes three steps in the polymeric membranes: "absorption" of molecules on the surface, their "diffusion" inside, and their "desorption" of molecules on the low-pressure side [52]. The transport of gas through polymeric membranes is subjected to various polymer characteristics including the composition, mean molecular weight, distribution of the molecular weight, polymer polarity, cross-linking, degree of crystallization, glass transition temperature, intersegmental chain spacing (d-spacing), thermal processing history, free volume content, morphology, orientation, defects, crystalline types, and so on. The existence of crystalline fields in a polymer facilitates the attachment between tortuosity and gas diffusion, making the gas transport quite complex. The free volume existing in polymers is able to be conceived in the form of micro voids or apertures scattered in the polymeric matrix. The condensability of penetrants is measured based on the boiling point, critical temperature, and Lennard-Jones

potential force constant of the penetrants. The chemical affinity describes the interplay between the gas-polymeric matrices. In addition, the interplay between gas and the functional groups of a polymer leads to the greater gas solubility in the polymer. Thus, CO₂ can be considerably soluble in polar polymers, because it has a quadrupolar moment. Also, condensability contributes

towards the gas permeation via polymeric membranes. Table 2 presents the physical specifications, including the condensability, of CO₂, CH₄, N₂, O₂, and H₂ [63-79]. Glassy and rubbery polymers separate gases, principally by size and condensability respectively. Gas molecules with relatively small sizes and higher condensabilities have higher permeabilities.

Table 2

Physical specifications of CO₂, CH₄, N₂, O₂, and H₂ [63].

Physical specifications	Gas molecules				
	CO ₂	CH ₄	N ₂	O ₂	H ₂
Molecular weight	44.01	16.04	28.01	31.99	2.02
Kinetic diameter (Å)	3.3	3.8	3.64	3.46	2.89
Density at 0 °C, 1 atm., (g/L)	1.977	0.72	1.25 ^a	1.429	0.0899
Critical temperature (°C)	31	-82.1	-147.1	-118.6	-240.2
Critical pressure (atm.)	72.9	45.8	33.5	49.77	12.8
Critical Density (g/mL)	0.468	0.162	0.311	0.436	0.031
Viscosity (at 21 °C, 1 atm., (cp)	0.0148	0.0106 ^b 0.0116 ^c	0.017 0.0174	0.019 ^d	0.0087 ^e
	^a At 20 °C	^b At 4.4 °C	^c At 37.8 °C	^d At 0 °C	^e At 15 °C

4. Mixed matrix membranes (MMMs)

Hybrid or mixed matrix membranes represent a set of distinct polymer-based membranes of which each comprises a continuous polymer phase, a discrete inorganic phase, and an organic-inorganic interphase [84]. Usually, the inorganic phase is assumed to be in the form of nano- and micro-level materials referred to as additives or fillers. The concept of MMMs was first originated following the incorporation of zeolite 5A molecular sieves into the PDMS matrix for the gas separation in 1973 [85, 86]. Inorganic materials' own merits mostly include the good rigidity, high thermal stability, and resistance to chemicals and harsh environments [87]. Different types of

traditional inorganic materials, e.g., metal oxide, silica, zeolites, and carbon molecular sieves, were used to form and enhance MMMs. Such membrane types can potentially attain higher selectivity, permeability, or both, proportionately to the prevailing polymeric membranes, produced by adding inorganic particles with their innate high separation features [63, 88, 89]. With the combination of inorganic fillers and polymer matrices, MMMs can circumvent the restrictions of inorganic membranes while demonstrating different perm-selective properties of polymers and inorganic fillers [90].

Based on the compatibility between the matrix and the filler, four different cases

(Figure 1) and the supposed impacts on the separation characteristics of the membrane can be explained [91-95]. Case 1 represents a perfect scenario where the filler is completely combined with the polymer matrix. Modifying the filler surface with suitable agents caused strong adhesion between polymer matrix and molecular sieve phases. The voids between polymer and molecular sieve phases are filled by low molecular weight materials. In most occasions, high processing temperatures close to the glass transition temperature (T_g , the temperature at or above which the molecular structure exhibits macromolecular mobility) of polymeric materials are applied to maintain the polymer chain flexibility during the membrane

formation. The result of this case scenario is the upgraded separation of MMMs. Case 2 represents the polymer matrix rigidification in a region close to the filler. This ordinarily leads to the improvement of the selectivity due to high rigidity but also low permeability. This finding can be verified by an increase in the glass transition temperature of MMMs. Case 3 shows an interface because of the lack of harmony between the particle and the polymer matrix, leading to the permeability escalation resulted from the greater fractional free volume and lower selectivity. In Case 4, the polymer matrix pierces into the free volume of the filler or the pore. Herein, both selectivity and permeability are reduced.

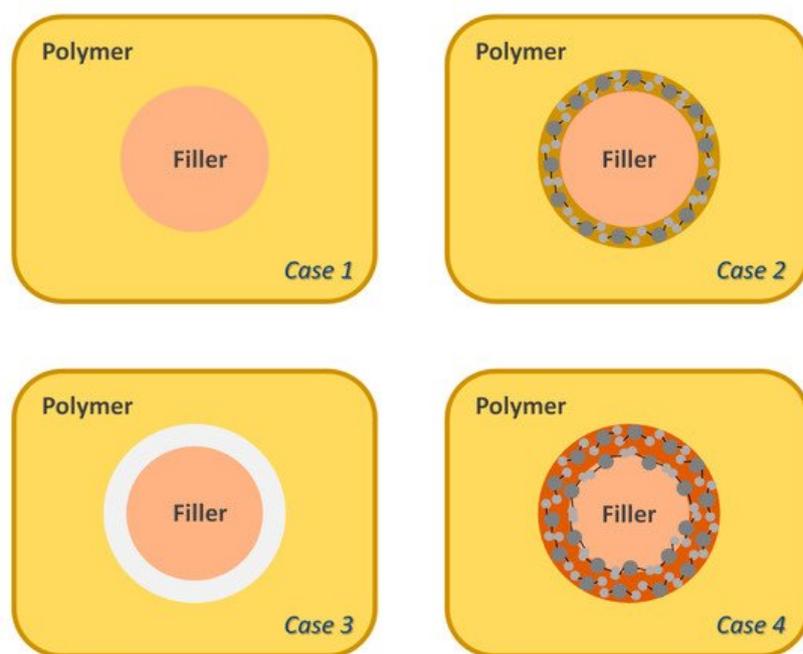


Figure 1. Schematic diagram of different MMM structures [96, 97].

5. Inorganic micro- and nano-fillers

The inorganic fillers to be used in mixed-matrix membranes (MMMs) should have (1) great affinity to the polymer, (2) matching gas transport properties, (3) particles as small as required, since the selective layers of modern polymer-based gas separation membranes have a thickness of 100 nm and less [97]. Some

fillers have been studied in order to be combined with a polymer matrix, carbon mesoporous silica and zeolites [98-104].

Porous inorganic fillers provide molecular sieves, separating gases by their shape or size, so that high gas permeabilities and desired component selectivities are attained. A non-porous inorganic filler reduces the diffusion of

larger molecules and increases the matrix tortuous pattern [105, 106]. The presence of nano-sized inorganic materials may change the polymer packing chain by growing the void volume. Some of the key benefits of incorporating microporous nanomaterials, such as conventional fillers (zeolites, silicas, metal oxides) and unconventional nanofillers (graphenes, CNTs, ZIFs), into the polymer matrix to form MMMs include the intensified mechanical and chemical performance of polymers coupled with the upgraded gas separation efficiency, the ability to combine the simplicity of casting and processability, modifiable surface functionalities, lofty surface areas of microporous nanomaterials and adjustable pore dimensions [107]. Many polymers have been studied to fabricate MMMs by adding inorganic fillers like nonporous silica [108, 109], structured mesoporous silica [110-112], carbon molecular sieves [113], carbon nanotubes [114, 115], zeolites [116], and microporous nanomaterials [117] for the design of efficient composite membranes, which show better separation performance compared to pure polymer membranes. Among porous materials, carbon molecular sieves (CMS) and zeolites are the most commonly used inorganic fillers for the MMM enhancement [118-123]. CMSs are able to effectively divorce the gas molecules with highly similar sizes. From decades ago, CMSs have been obviously proven to be very effective for the gas separation in the adsorption application due to their better absorptivity for some particular gases [124, 125].

Zeolite molecular strainers are perfect materials with significantly higher diffusivity and selectivity compared with polymeric materials. The precise shape and size discrimination resulted from the slender pore

distribution ensures the superior selectivity. Nonetheless, zeolite membranes are pricey and have difficulties in forming continual and defect-free membranes for practical applications [126-129]. One of the major problems of zeolite-based MMMs is that they usually demonstrate poor polymer-filler compatibility, resulting in the formation of defective membranes with non-selective voids at the polymer-filler interface [130]. In this regard, the outcome of the use of MOFs as fillers might be a breakthrough in the MMM field, as their partially organic nature supply an enhanced polymer-filler adhesion, hindering the resulted membranes to underperform [131, 132].

Activated carbon is a good instance of large pore size inorganic fillers. Adding inflexible materials with big pore sizes (the pore dimensions much larger than those of the penetrants) into the polymer matrix can cause the selective surface flow of specific components in the pores of the particles. In this instance the more condensable or adsorbable constituent can be adsorbed and spread out selectively via the particles and so the less adsorbable component permeates slower [124-133].

Amid different fillers, carbon nanotubes (CNTs) are fundamentally new nano-porous material having the potential to be over the Robeson's upper bound [134, 135]. These fillers have been widely applied because of their diffusivity, their affinity to small molecules, such as CH₄, CO₂ and others gases, and also due to their ability to resist high temperatures and aggressive chemicals [136]. The properties of polymer nanocomposites including carbon nanotubes depend on several factors in addition to the polymer: the synthetic process used to construct nanotubes; nanotube purification process (if any); total and type of

impurities in the nanotubes; nanotubes orientation in the polymer matrix; length, diameter and aspect ratio of the nanotube objects in the composite (ropes, isolated and/or bundles) [137-139]. Anyway, it should be noted that carbon nanotubes are still highly expensive and may have dangerous to health effects due to their fast migration speed.

Graphene, is a two-dimensional sp^2 -carbon sheet constituted of a long-range conjugation over its honeycomb aromatic framework [140]. As the pores are unavoidable for the gas transportation, a great number of theoretical studies explored the transport of different gases by way of single-layered graphene and its pore functionalized derivatives [141]. The Nanoporous graphene (NPG) with the specific pore size and geometry would be a very

efficient gas separation membrane, as the research results show. In 2009, Jiang et al. found a high selectivity in the order of 108 through a N-functionalized pore and an extremely high selectivity in the order of 1023 through an all-H passivated pore for separating H_2/CH_4 mixtures with a high H_2 permeance (Figure 2a). The selectivity of H_2 over several other gas molecules that often accompany H_2 in industrial steam methane reforming or dehydrogenation of alkanes (such as N_2 , CO , and CH_4) is sensitive to the pore size of the membrane (Figure 2b). An ion-gated graphene membrane comprising a monolayer of ionic liquid-coated porous graphene would be able to dynamically modulate the pore size to achieve the selective gas separation (Figure 2c).

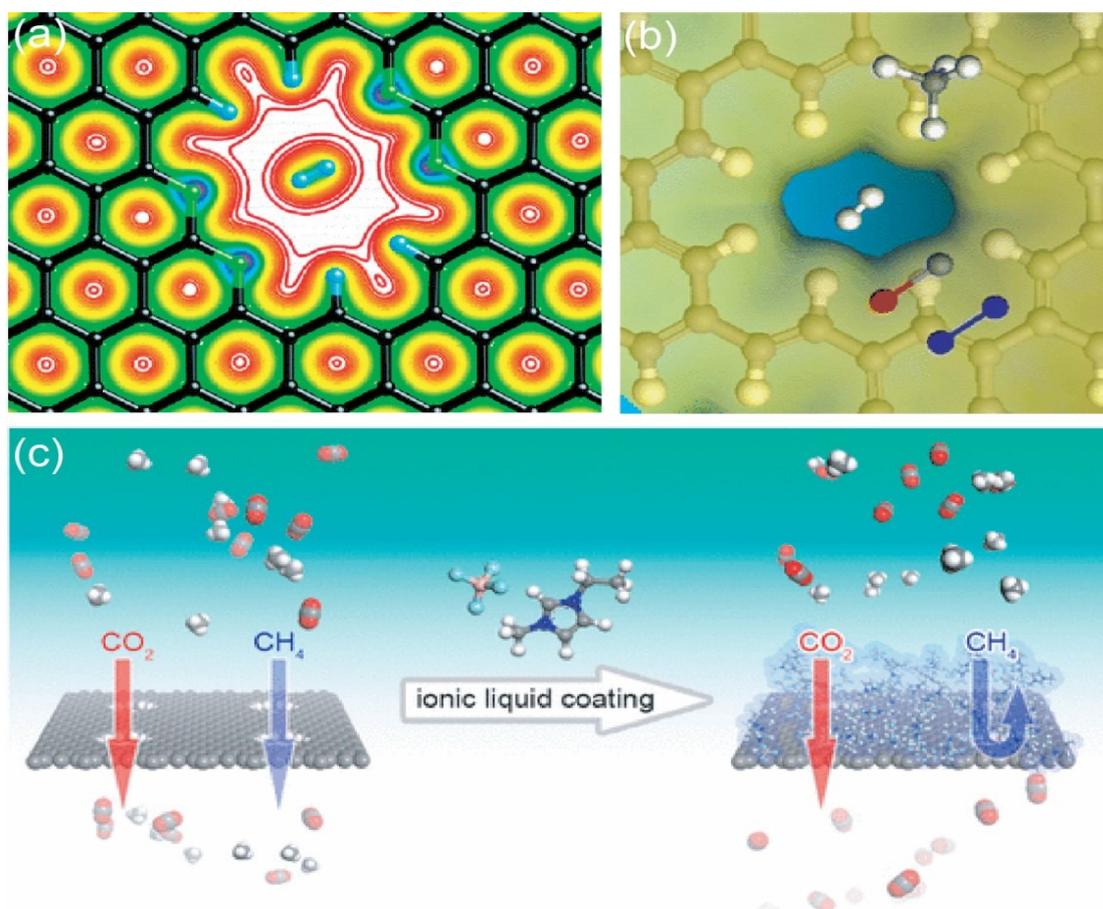


Figure 2. (a) H_2 separation through the monolayer graphene having N-functionalized pores; [141], (b) Selective passage of H_2 through the single-layered porous graphene; [142], (c) Schematic illustration of the selective CO_2 separation by the ionic-liquid coated porous graphene monolayer [143].

Silica is an inorganic filler that has attracted prominent attention all over the MMM expansion. Silica particles can be categorized into various types with regard to their pore and particle sizes. Each type of silica has a distinct effect of the chemical, physical and gaseous transfer mechanism of a normal polymeric membrane [107].

Silica nanoparticles can be more categorized as non-porous silica and mesoporous silica. Ordered mesoporous silica with the diversity of shape, pore diameter and particle size is another form of silica which has been potentially used for the developing of a new generation of MMM. Mesoporous molecular sieves possess pores big enough (2-50 nm) to freely allow the penetration of polymer chains, resulting in the better dispersion of particles and wetting [144]. Ordered mesoporous silica materials have properties such as high thermal and mechanical stability, high specific surface areas ($> 500 \text{ m}^2/\text{g}$), Feasibility of Structural changes in the molecule [98]. The most frequently ordered mesoporous silica fillers are SBA-15, MCM-41 and MCM-48 [125, 145-148].

6. Metal-organic frameworks (MOFs)

Another class of porous materials that has been used in MMMs is the metal-organic frameworks (MOFs) including transition metals and transition metal oxides linked by organic ligands for making one, two, and three-dimensional microporous structures. MOFs are being studied extensively because of their functionalizable pore walls, exceptionally high surface region, flexible chemical composition, affinity for specific gases and controlled porosity due to modifiable organic linking units and the presence of strong chemical bonds [149]. These properties make them promising

materials for being used in catalysis, gas storage and separation processes [150]. For gas storage and separation purposes, MOFs can react as molecular sieves due to their inflexible frameworks and limited pore sizes, allowing the size exclusion of gas molecules [151, 152].

MOFs have excessive sorption capacities and display sorption selectivity among various gasses due to affinity effects and size exclusion, thus making them viable for industrial use cases, including carbon dioxide and hydrogen storage and adsorbers/desorbers [153-157]. Moreover, the mentioned characteristics make them alluring as membrane materials [158-160]. Despite the significant permeability improvements explored for MOF-MMMs, the selectivity improvement demands greater attention [161, 162]. Until now, MOF membranes, similar to other inorganic membranes, remain too costly to produce and have low mechanical stability [163].

Zeolitic imidazolate frameworks (ZIFs) include a subset of MOFs with outstanding chemical and thermal stability [164, 166, 167]. The ZIFs framework structure includes transition metal (e.g. Co, Zn) cations bonded via anionic imidazolate bonds. In addition, the pore size adsorption features of ZIFs are changed by modifying or chemically changing the anionic imidazolate bond [167]. Latest findings demonstrate that ZIFs are of the molecular sieving characteristics similar to those of zeolites [164-168], proving them to be hopeful candidates for the MMM development. Findings regarding molecular sieve membranes associated with several ZIFs illustrate the role of this material in the gas separation [169-174].

ZIF-8, one of the most extensively studied ZIFs, was originally synthesized as microcrystals by Yagui and colleagues using

dimethylformamide (DMF) [175]. ZIF-8 appears to be characterized by a sodalite zeolite-like topology with a cubic space group of $I\bar{4}3m$ [176]. Figure 3 shows that four N atoms of 2-methylimidazolate and each Zn metal are tetrahedrally correlated. The sodalite cages are 11.6 Å in diameter connected by means of small apertures with 3.4 Å diameters. Nonetheless, the ZIF-8 structure has an assured flexibility, mainly due to the reorientation of the imidazolate ring allowing the apertures to vary in size.

Metal oxide nanoparticles such as TiO_2 and MgO are emerging materials because of their potential applications for membrane-based separation purposes. The primary particles of these metal oxides, with high specific areas and diameters in nanoscale, permit upgrade in the particle distribution and disallow the non-

selective void formation on the nanoparticles/polymer matrix interface. So, these nanoparticles are not intrinsically fused together and have the potential to be dispersed individually or collectively at nanoscales [125-177].

One set of highly investigated MOFs in terms of transition metals are MIL-type materials. MIL denotes Materials Institute Lavoisier, a region where these MOFs were initially synthesized by Ferey's association [178]. The highly typical MILs are MIL-53, MIL-100 and MIL-101, of which all are generally comprised of trivalent metals (iron, aluminum, vanadium, chromium, etc.) and trimellitic acid, terephthalic acid and other ligands or modified ligands, which may establish different pore structures with satisfactory structural stabilities [179].

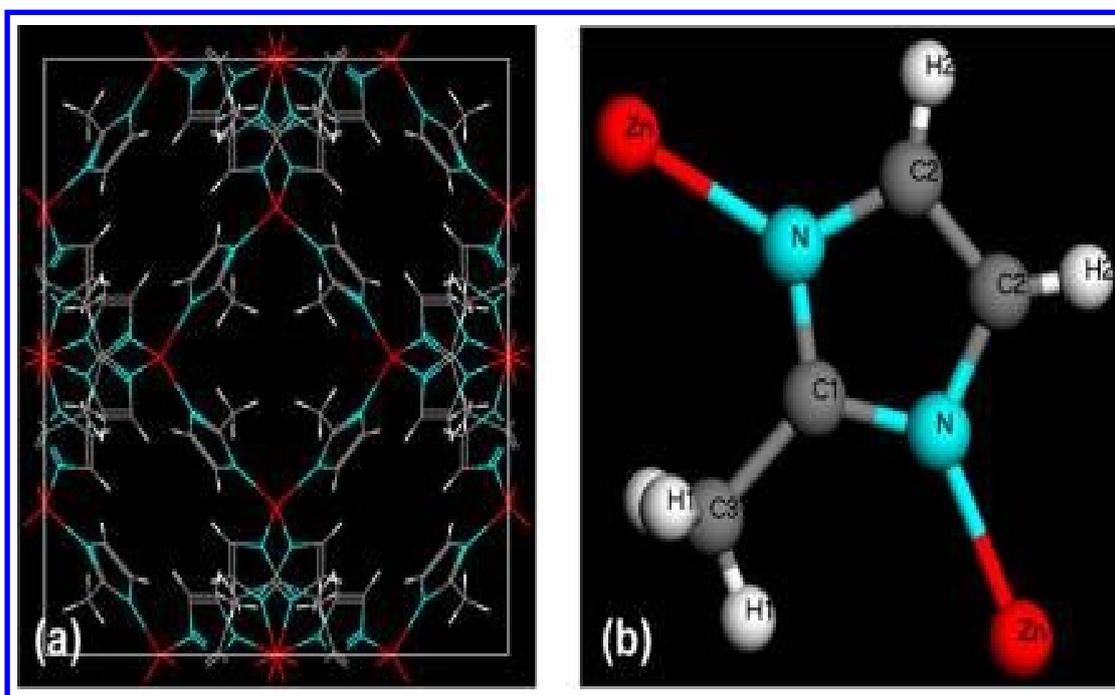


Figure 3. (a) Unit cell and (b) atomic types of ZIF-8 [177].

As exemplified in Figure 4, MIL-100 (Fe) and MIL-101 (Fe) display 3D structures. MIL-100 (Fe) enjoys water and thermal stability [180], while MIL-101 (Fe) can be converted

into MIL-53 or MIL-88 in strong polar solvents [181, 182]. Moreover, MIL-100 appears to be having higher water stability than UiO and ZIF [183-185].

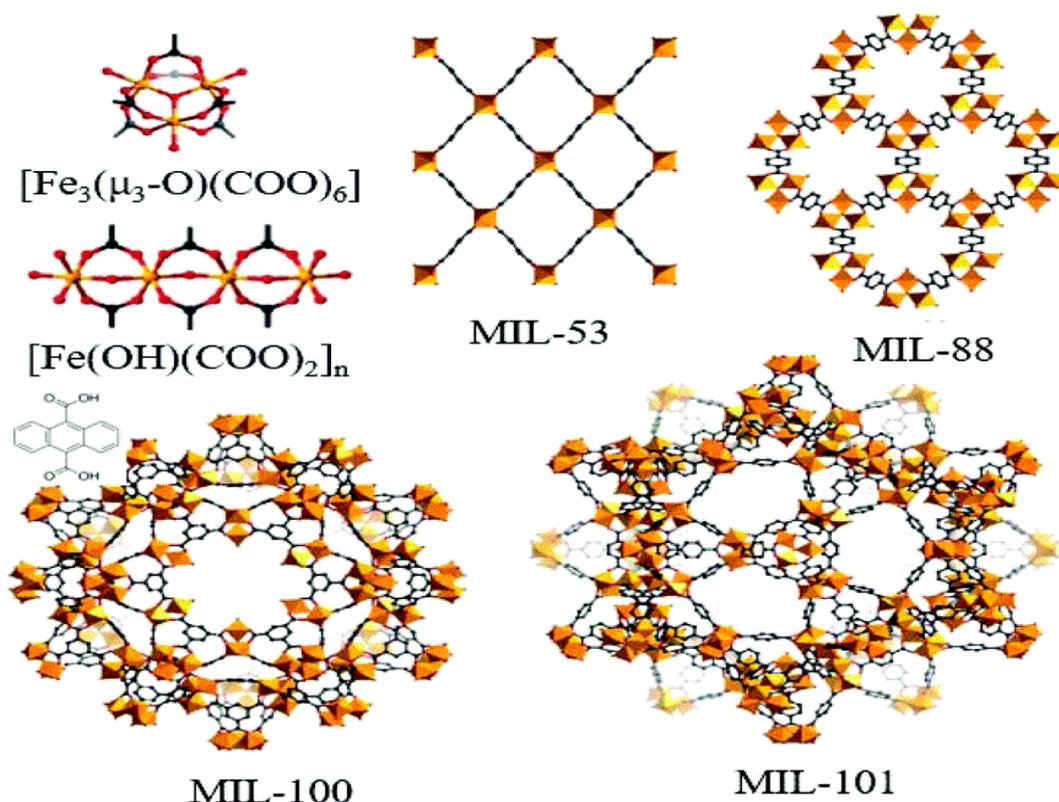


Figure 4. Structures of the metal clusters and representative MIL series of Fe-MOFs [180].

Whereas MOFs are investigated and employed by researchers of various interests, the UiO family (featuring UiO-66, UiO-67, and UiO-68) representing the various offered series, are three-dimensional porous materials made of Zr^{4+} and dicarboxylic acids. UiO-66 resembles their most outstanding member, that is also considered as the prototype of this subfamily of MOFs because other UiOs are isoreticularly derived from UiO-66 [186]. Nevertheless, UiO-66 (and isoreticular UiO-67 and UiO-68) represents a zirconium-based MOF featuring quite a large surface district (1180-1240 m^2/g) and supreme stability. Developed by Prof. Karl Petter Lillerud of the Department of Chemistry at the University of Oslo, UiO-66 includes $\text{Zr}_6\text{O}_4(\text{OH})_4$ octahedra that are 12-fold bound to next octahedra via a 1,4-benzene-dicarboxylate (BDC) linker, leading to a highly wrapped FCC structure. The Zr-O bonds established between the cluster and carboxylate ligands are identified as the source

of the higher stability of Zr-based MOFs. Particularly, the mixture of strong Zr-O bonds and the capability of the inner Zr_6 -cluster to be rearranged in a reverse manner upon addition or removal of $\mu^3\text{-OH}$ groups in need of any changes in the connecting carboxylates are ideas that reinforce the better stability of UiO-66 [187].

Amid metal organic frameworks, Cu-BTC can be among the best and promising materials for being used in technological applications [188-193]. Cu-BTC, also called HKUST-1, is constituted of benzene-1, 3, 5-tricarboxylate (BTC) ligands coordinating copper ions and forming big cavities and small octahedral cages that are available to small molecules by means of small windows [194]. The big and small cages are almost 9 and 5 Å in diameter respectively, and the triangular window that attaches both kinds of cages is about 3.5 Å in diameter. Figure 5 gives the isocontour image of the energy outlook for Cu-BTC.

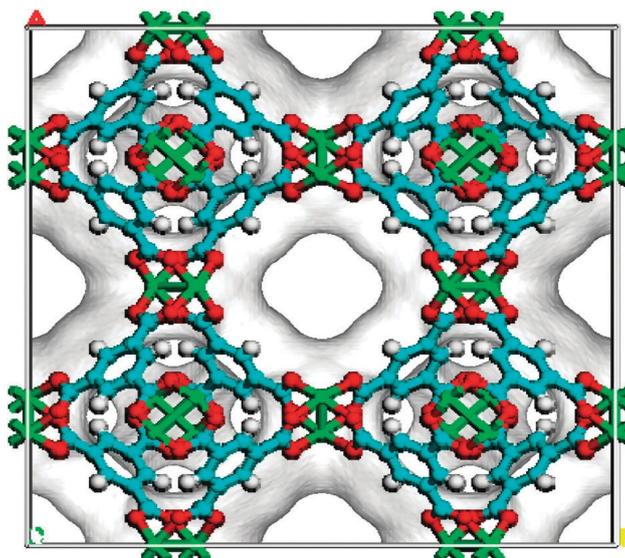


Figure 5. Isocontour image of the energy prospect of Cu-BTC illustrating the large central cages (about 9 Å diameter) and small octahedral cages (about 5 Å diameter) bound by the windows of B 3.5 Å in diameter. The atomic structure is superimposed. The carbon atoms are plotted in blue, the hydrogen atoms in white, and the oxygen and the copper atoms in red and green respectively [194].

Because experimental statistics are inaccessible, molecular simulation can turn into an essential method to forecast adsorption and clarify the separation mechanisms occurring in the pores [193, 195-199]. The major benefits of applying computational methods are that simulations supply exclusive microscopic perception and complete the control of the conditions. Moreover, simulations are inexpensive, facilitate investigating hypothetical structures, are used as a forecast tool, and represent a better complement to the experimental work.

7. Future direction

The enhancement of the application and the fabrication of MMMs involving inorganic particles in the polymer for the gas separation remain yet quite less than those for orderly polymeric membranes, paving the way for further development. More than a few materials, including metal-organic frameworks, carbon nanotubes, activated carbons, meso-porous materials, zeolites and carbon molecular sieves, are applied to MMMs

at the inorganic phase. Although these materials are quite viable for being used in MMM applications, many difficulties remain to be solved.

The complicated states at the interface, which connects the polymer to particles, make the MMMs fabrication process difficult to control. The mechanisms underlying these phenomena need to be extensively studied. The recent molecular dynamic simulations of MMM show the decreased permeability and polymer chain mobility near the interface. Forming nano-sized fillers without agglomeration and obtaining their separation characteristics are essential to the next generation of MMMs. In simple terms, nano-sized particles facilitate forming thin membrane layers and are distributed more uniformly than micro-size particles. Smaller particles can present a polymer/particle interfacial region that promotes the contact for the polymer-filler interface. Further, nano-sized fillers simply migrate to the outermost selective skin layer through spinning the hollow fiber. Another important point is that

when the size is scaled down to these values, the morphology and shape of the particles of the material can be significantly altered, so that the property changes will affect the membrane performance.

8. Conclusions

The membrane technology offers greater efficiency, simpler configuration, and lower operating and capital costs than traditional separation processes such as the cryogenic distillation, adsorption and low-temperature condensation. Anyway, it was found that the performance of the membrane polymers (so-called Robeson upper limit) are restricted because of the inverse relation between selectivity and permeability, i.e., the most important gas separation parameters in membranes. To resolve the issue, new procedures and materials for the membrane fabrication are being evaluated. Especially, MMMs by incorporating fillers such as metal-organic frameworks, MOF-silicate hybrids, layered silicates, zeolites and carbon-based materials have functioned better than pure polymers, reaching or exceeding the Robeson limit. MOFs are promising novel adsorbents for capturing gas because of their great pore volumes, high surface regions, simple controllable compositions and pore structures. It has been found that the correct interaction between fillers and polymers greatly improves the separation performance of membranes. The results also showed that MOF fillers improve the selectivity and permeability over other fillers.

Acknowledgement

This manuscript is prepared based on the Ph. D. thesis of the first author at Rasht Branch, Islamic Azad University, Rasht, Iran.

References

- [1] Baker, R. W., Membrane technology and applications, 1st edition, McGraw-Hill, New York, USA, (2000).
- [2] Baker, R. W., Membrane technology and applications, 2nd edition, John Wiley & Sons, New York, USA, (2004).
- [3] Ismail, A., Khulbe, K. C. and Matsuura, T., Gas separation membranes: Polymeric and inorganic, Springer, (2015).
- [4] Stewart, M. and Arnold, K., Gas sweetening and processing field manual, Gulf Professional Publishing, (2011).
- [5] Ismail, A. and Matsuura, T., Sustainable membrane technology for energy, water, and environment, John Wiley & Sons, (2012).
- [6] Ball, P., "Scale-up and scale-down of membrane-based separation processes", *J. Membr. Technol.*, **117**, 10 (2000).
- [7] Ramírez-Santos, Á. A., Castel, C. and Favre, E., "A review of gas separation technologies within emission reduction programs in the iron and steel sector: Current application and development perspectives", *Sep. Purif. Technol.*, **194**, 425 (2018).
- [8] Buonomenna, M. G., "Membrane processes for a sustainable industrial growth", *RSC Advances.*, **3**, 5694 (2013).
- [9] Baker, R. W. and Low, B. T., "Gas Separation Membrane Materials: A Perspective", *Macromolecules.*, **47**, 6999 (2014).
- [10] Low, Z. X., Budd, P. M., McKeown, N. B., Patterson, D. A., "Gas Permeation Properties, Physical Aging, and Its Mitigation in High Free Volume Glassy Polymers", *Chem. Rev.*, **118**, 5871 (2018).
- [11] Galizia, M., Chi, W. S., Smith, Z. P., Merkel, T. C., Baker, R. W., Freeman, B. D., "50th Anniversary Perspective:

- Polymers and Mixed Matrix Membranes for Gas and Vapor Separation: A Review and Prospective Opportunities”, *Macromolecules.*, 50, 7809 (2017).
- [12] Kesting, R. E. and Fritzsche, A. K., *Polymeric Gas Separation Membranes*, Wiley, New York, NY, 1993).
- [13] Paul, D. R. and Yampol'skii Y. P., *Polymeric Gas Separation Membranes*. 1st ed, CRC Press, Boca Raton, FL, 1994).
- [14] Spillman, R.W., “Economics of gas separation membranes”, *Chem. Eng. Prog.*, 85, 41 (2008).
- [15] Stern, S. A., “Polymers for gas separations: the next decade”, *J. Membr. Sci.*, 94, 1 (1994).
- [16] Koros, W. J. and Story B. J. Jordan S. M. O'Brien, K. Husk, G. R., “Material selection considerations for gas separation processes”, *Polym. Eng. Sci.*, 27, 603 (1987).
- [17] Koros, W. J. and Mahajan, R., “Pushing the limits on possibilities for large scale gas separation: which strategies?”, *J. Membr. Sci.*, 175, 181 (2000).
- [18] Fane, A. G. Wang, R. Hu, M. X., “Synthetic membranes for water purification: Status and future”, *Angew. Chem. Int. Ed. Engl.*, 54, 3368 (2015).
- [19] Werber, J. R., Osuji, C. O. and Elimelech, M., “Materials for next-generation desalination and water purification membranes”, *Nat. Rev. Mater.*, 1, 1 (2016).
- [20] Ong, Y. K. Shi, G. M. Le, N. L. Tang, Y. P. Zuo, J. Nunes, S. P. Chung, T.-S., “Recent membrane development for pervaporation processes”, *Prog. Polym. Sci.*, 57, 1 (2016).
- [21] Bernardo, P. Drioli, E., “Golemme G. Membrane Gas Separation: A Review/State of the Art”, *Ind. Eng. Chem. Res.*, 48, 4638 (2009).
- [22] Robb W. L., Thin silicone membranes—their permeation properties and some applications. *Annals of the New York Academy of Sciences*. 1968;146:119–137.
- [23] George, G. Bhorla, N. Alhallaq, S. Abdala, A. Mittal, V., “Polymer membranes for acid gas removal from natural gas”, *Sep and Purif Technol.*, 158, 333 (2016).
- [24] Guiver, M. D. and Lee, Y. M., “Polymer rigidity improves microporous membranes”, *Science.*, 339, 284 (2013).
- [25] Henis, J. M. S. Trinodi, M. K., “A novel approach to gas separations using composite hollow fiber membranes”, *Separation Science and Technology.*, 15, 1059 (1980).
- [26] Baker, R. W., “Future directions of membrane gas separation technology”, *Industrial and Engineering Chemistry Research.*, 41, 1393 (2002).
- [27] George, G. Bhorla, N. Alhallaq, S. Abdala, A. Mittal, V., “Polymer membranes for acid gas removal from natural gas”, *Separation and Purification Technology.*, 158, 333 (2016).
- [28] Bernardo, P., Drioli, E., Golemme, G., “Membrane gas separation: a review/state of the art”, *Industrial and Engineering Chemistry Research.*, 48, 4638 (2009).
- [29] Membrane Research and Technology (MTR), (<http://www.mtrinc.com>).
- [30] U.S. Department of Energy, “Membrane system for the recovery of volatile organic compounds from remediation off-gases,” *Innovative Technology Summary Report*, U.S. Department of Energy, 2001.
- [31] Zimmerman, C. M. Singh, A. Koros, W. J., “Tailoring mixed matrix composite

- membranes for gas separations”, *J. Membr. Sci.*, 137, 145 (1997).
- [32] Li, Y. Chung, T. S., Cao, C. Kulprathipanja, S., “The effects of polymer chain rigidification, zeolite pore size and pore blockage on polyethersulfone (PES)-zeolite A mixed matrix membranes”, *J. Membr. Sci.*, 260, 45 (2005).
- [33] Guan, H. M. Chung, T. S. Huang, Z. Chng, M. L. Kulprathipanja, S., “Poly(vinyl alcohol) multilayer mixed matrix membranes for the dehydration of ethanol-water mixture”, *J. Membr. Sci.*, 268, 113 (2006).
- [34] Kim, S. Pechar, T. W. Marand, E.,” Poly(imide siloxane) and carbon nanotube mixed matrix membranes for gas separation “, *Desalination.*, 192, 330 (2006).
- [35] Jiang, L. Y. Chung, T. S. Cao, C. Huang, Z. Kulprathipanja, S., “Advances in Functional Separation Membranes”, *J. Membr. Sci.*, 252, 89 (2005).
- [36] Okumus , E. Gurkan, T. Yilmaz, L., “Development of a Mixed-Matrix Membrane for Pervaporation”, *Sep. Sci. Technol.*, 29, 2451 (1994).
- [37] Li, Y. Chung, T. S. Kulprathipanja, S., “Novel Ag⁺-zeolite/polymer mixed matrix membranes with a high CO₂/CH₄ selectivity”, *AIChE J.*, 53, 610 - 616 (2007).
- [38] Jia, M. D. Peinemann, K. V. Behling, R. D., “Molecular sieving effect of the zeolite-filled silicone rubber membranes in gas permeation”, *J. Membr. Sci.*, 57, 289 (1991).
- [39] Shao, L. Samseth , J. Hagg, M. B., “Crosslinking and stabilization of nanoparticle filled PMP nanocomposite membranes for gas separations”, *J. Membr. Sci.*, 326, 285 (2009).
- [40] Nunes, S. P. Peinemann, K. V. Ohlrogge, K. Alpers, A. Keller, M. Pires, A. T. N., “Membranes of poly(ether imide) and nanodispersed silica”, *J. Membr. Sci.*, 157, 219 (1999).
- [41] Sforca M. L. Yoshida, I. V. P. Nunes, S. P., “Organic–inorganic membranes prepared from polyether diamine and epoxy silane”, *J. Membr. Sci.*, 159, 197-207 (1999).
- [42] Zoppi, R. A., Neves das , S. Nunes, S. P., “Hybrid films of poly(ethylene oxide-b-amide-6) containing sol–gel silicon or titanium oxide as inorganic fillers: effect of morphology and mechanical properties on gas permeability”, *Polymer.*, 41, 5461 (2000).
- [43] Li, W. X. Zhang, X. J. Xing, W. H. Jin, W. Q. Xu, N. P., “Hydrolysis of Ethyl Lactate Coupled by Vapor Permeation Using Polydimethylsiloxane/Ceramic Composite Membrane”, *Ind. Eng. Chem. Res.*, 49, 11244 (2010).
- [44] Xiangli, F. J. Chen, Y. W. Jin, W. Q. Xu, N. P., “Polydimethylsiloxane (PDMS)/Ceramic Composite Membrane with High Flux for Pervaporation of Ethanol–Water Mixtures”, *Ind. Eng. Chem. Res.* 46, (2007).
- [45] Kulprathipanja, S. Neuzil, R. W. Li, N. N., “Separation of fluids by means of mixed matrix membranes”, *US Pat.* 4740219, 1988.
- [46] Chung, T. S. Jiang, L. Y. Li, Y. Kulprathipanja, S., “Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation”, *Prog. Polym. Sci.*, 32, 483 (2007).
- [47] Aptel, P. Armor, J. Audinos, R. Baker, R. W. Bakish, R. Belfort, G. Bikson, B.

- Brown, R. G. Bryk, M. Burke, J. J., "Terminology for membranes and membrane processes (IUPAC Recommendations 1996)", *J. Membr. Sci.*, 120, 149 (1996).
- [48] Ter Minassian-Saraga, L. Adler, M. Barraud, A. Churaev, N. V, Eaton, D. F. Kuhn, H. Misono, M. Platikanov, D. Ralston, J. Silberberg, A., "Thin films including layers: Terminology in relation to their preparation and characterization. IUPAC recommendations 1994", *Thin Solid Films.*, 277, 7 (1996).
- [49] Baker, R. W., *Membrane technology and applications*, 3rd edition, John Wiley & Sons, New York, USA, (2012).
- [50] Ho, W. S. Sirkar, K. K., editors. *Membrane Handbook*. Van Nostrand Reinhold; New York, NY, USA, 1992.
- [51] Bodzek, M. Bohdziewicz, J. Konieczny, K., *Techniki Membranowe W Ochronie Środowiska*. Wydawnictwo Politechniki Śląskiej; TECHNIKI MEMBRANOWE W OCHRONIE ŚRODOWISKA. Gliwice, Poland, 1997.
- [52] Mulder, M. H. V., *Basic Principles of Membrane Technology*. Kluwer Academic Publishers; Dordrecht, The Netherlands: Boston, MA, USA: London, UK, 1991.
- [53] Feng, X. Huang, R. Y. M., "Liquid separation by membrane pervaporation: A review.", *Ind. Eng. Chem. Res.*, 36, 1048 (1997).
- [54] Slater, C. S., "A review of: "Pervaporation membrane separation processes", *Sep. Purif. Methods.*, 20, 109 (1991).
- [55] Basile, A. Gallucci, F., *Membranes for Membrane Reactors: Preparation, Optimization and Selection*. John Wiley & Sons, 2011.
- [56] Nandi, B. K. Uppaluri, R., Purkait, M. K., "Preparation and characterization of low cost ceramic membranes for micro-filtration applications", *Applied. Clay. Science.*, 42, 102 (2008).
- [57] Green, D., Perry, R., *Perry's Chemical Engineers' Handbook*, McGraw-Hill Education, 8th edition, 2007.
- [58] Gandia, L. Arzamedi, G. Dieguez, P., "Renewable Hydrogen Technologies: Production, Purification, Storage", *Applications and Safety*, Elsevier Science, 2013.
- [59] Lin, H. Gupta, R. P., "Plasticization-enhanced hydrogen purification using polymeric membranes", *Science.*, 311, 639 (2006).
- [60] Park, H. B., Jung, C. H., Lee, Y. M., Hill, A. J., Pas, S. J., Mudie, S. T., Van Wagner, E. Freeman, B. D. Cookson, D. J., "Polymers with cavities tuned for fast selective transport of small molecules and ions", *Science.*, 318, 254 (2007).
- [61] Japip, S., Liao, K. S., Chung, T. S., "Molecularly tuned free volume of vapor cross-linked 6FDA-Durene/ZIF-71 MMMs for H₂/CO₂ separation at 150 °C", *Adv. Mater.*, 29, (2017).
- [62] Yong, W. F. Li, F. Y. Chung, T. S. Tong, Y. W., "Highly permeable chemically modified PIM-1/Matrimid membranes for green hydrogen purification", *J. Mater. Chem.*, 1, 13914 (2013).
- [63] Shekhawat, D. Luebke, D. R. Pennline, H. W., "A review of carbon dioxide selective membranes, A Topical Report", *National Energy Technology Laboratory United States Department of Energy.*, 1, (2003).
- [64] Hsieh, H. P., "Membrane and Membrane Processes, in *Inorganic Membranes for Separation and Reaction*. Elsevier,

- Amsterdam, 1996.
- [65] Burggraaf, A. J. Keizer, K., "Inorganic Membranes: Synthesis, Characteristics, and Applications", Van Nostrand Reinhold, New York, 10 (1991).
- [66] Pabby, A. K. Rizvi, S. S. H. Sastre, A. M., Handbook of Membrane Separations: Chemical, Pharmaceutical, Food, and Biotechnological Applications, CRC Press/Taylor & Francis Group, New York, 2009.
- [67] George, G. Bhoria, N. AlHallaq, S. Abdala, A. Mittal, V., "Polymer membranes for acid gas removal from natural gas", Sep Purif Technol., 158, 333 (2016).
- [68] Alqaheem, Y. Alomair, A. Vinoba, M. Perez, A., "Polymeric gas-separation membranes for petroleum refining", Int J Polym Sci., 1 (2017).
- [69] Heo, J. Lee, B. Lim, H., "Techno-economic analysis for CO₂ reforming of a medium-grade landfill gas in a membrane reactor for H₂ production", J. Clean Prod., 172, 2585 (2018).
- [70] Han, Y. Ho, WSW., "Recent advances in polymeric membranes for CO₂ capture", Chinese J Chem Eng., 26, 2238 (2018).
- [71] Shen, Y. Lua, A. C., "Preparation and characterization of mixed matrix membranes based on PVDF and three inorganic fillers (fumed nonporous silica, zeolite 4A and mesoporous MCM-41) for gas separation", J. Chem Eng. 192, 201 (2012).
- [72] Lua, A. C, Shen, Y., "Preparation and characterization of polyimide-silica composite membranes and their derived carbon-silica composite membranes for gas separation", J. Chem Eng., 220, 441 (2013).
- [73] Loeb, S. Sourirajan, S. "Sea water demineralization by means of a semipermeable membrane", Advances in Chemistry., 38, 117 (1962).
- [74] Petheram, L., Acid Rain, Bridgestone Books, 2002.
- [75] Sidney, L. Srinivasa, S., "High flow porous membranes for separating water from saline solutions. US Patent. 3 (133,132) 1964.
- [76] Gantzel, P. K., Merten, U., "Gas separations with high-flux cellulose acetate membranes", Industrial & Engineering Chemistry., 9, 331 (1970).
- [77] Cowie, J., Polymers: Chemistry and Physics of Modern Materials, Taylor & Francis, 2nd ed, 1991.
- [78] Robeson, L. M. Liu, Q. Freeman, B. D. and Paul, D. R., "Comparison of transport properties of rubbery and glassy polymers and the relevance to the upper bound relationship", J. Membr. Sci., 476, 421 (2015).
- [79] Porter, M. C., Handbook of Industrial Membrane Technology. Noyes Publications, Park Ridge, 1988.
- [80] Sea, B. K., Kusakabe, K. Morooka, S., "Pore-Size Control and Gas Permeation Kinetics of Silica Membranes by Pyrolysis of Phenyl-Substituted Ethoxysilanes with Cross-Flow Through a Porous Support Wall", J. Membr. Sci., 130, 41(1997).
- [81] George, G. Bhoria, N. Alhallaq, S. Abdala, A. Mittal, V., "Polymer membranes for acid gas removal from natural gas", Separation and Purification Technology., 158, 333 (2016).
- [82] Ismagilov, Z. R., "Porous alumina as a support for catalysts and membranes. Preparation and study", Reaction Kinetics and Catalysis Letters., 60, 225 (1997).
- [83] Wijmans, J. G. Baker, R. W., "The

- solution-diffusion model: a review”, *Journal of Membrane Science.*, 107, 1 (1995).
- [84] Vinh-Thang, H. Kaliaguine, S., “Predictive models for mixed-matrix membrane performance: A review”, *Chem. Rev.*, 113, 4980 (2013).
- [85] Hussain, M. König, A., “Mixed-Matrix Membrane for Gas Separation: Polydimethylsiloxane Filled with Zeolite”, *Chem. Eng. Technol.*, 35, 561 (2012).
- [86] Goh, P. S. Ismail, A. F. Sanip, S. M. Ng, B. C. Aziz, M., “Recent advances of inorganic fillers in mixed matrix membrane for gas separation”, *Sep. Purif. Technol.*, 81, 243 (2011).
- [87] Goh, P. S. Ismail, A. F., “A review on inorganic membranes for desalination and wastewater treatment”, *Desalination.*, 434, 60 (2018).
- [88] Zimmerman, C. M., Singh, A., Koros, W. J., “Tailoring mixed matrix composite membranes for gas separations”, *J. Membr. Sci.*, 137, 145 - 154 (1997).
- [89] Noble, R.D., “Perspectives on mixed matrix membranes”, *J. Membr. Sc.*, 378, 393 (2011).
- [90] Dechnik, J. Gascon, J. Doonan, C. J. Janiak, C. Sumby, C. J., “Mixed-Matrix Membranes”, *Angew. Chem. Int. Ed.*, 56, 9292 (2017).
- [91] Bastani, D. Esmaili, N. Asadollahi, M., “Polymeric mixed matrix membranes containing zeolites as a filler for gas separation applications: A review”, *J. Ind. Eng. Chem.*, 19, 375 (2013).
- [92] Carreon, M. A., *Membranes for Gas Separations.*, Colorado School of Mines: Golden, CO, USA, 2018.
- [93] Liu, C. Greer, D. W. O’Leary, B. W., *Advanced materials and membranes for gas separations: The uop approach.* In *Nanotechnology: Delivering on the Promise Volume 2*; American Chemical Society: Washington, DC, USA, 1224, 119 (2016).
- [94] Dechnik, J. Gascon, J. Doonan, C. J. Janiak, C. Sumby, C. J., “Mixed-matrix membranes”, *Angew. Chem. Int. Ed.* 56, 9292 (2017).
- [95] Yang, Y. Chuah, C. Y. Nie, L. Bae, T. H., “Enhancing the mechanical strength and CO₂/CH₄ separation performance of polymeric membranes by incorporating amine-appended porous polymers”, *J. Membr. Sci.*, 569, 149 (2019).
- [96] Ansaloni, L. Deng, L., 7—advances in polymer-inorganic hybrids as membrane materials. In *Recent Developments in Polymer Macro, Micro and Nano Blends*, Cambridge, UK, 163 (2017).
- [97] Maghami, M., Abdelrasoul, A., *Zeolite Mixed Matrix Membranes (Zeolite-MMMs) for Sustainable Engineering.* West Virginia University: Morgantown, VA, USA, 2018.
- [98] Li, Y. He, G. Wang, S. Yu, S. Pan, F. Wu, H. Jiang, Z., “Recent advances in the fabrication of advanced composite membranes”, *J. Mater. Chem.*, 1, 10058 (2013).
- [99] Liu, Y. Liu, G. Zhang, C. Qiu, W. Yi, S. Chernikova, V. Chen, Z. Belmabkhout, Y. Eddaoudi M., “Enhanced CO₂/CH₄ separation performance of a mixed matrix membrane based on tailored mof-polymer formulations”, *Adv. Sci.*, 5, 1800982 (2018).
- [100] Bae, T. H. Liu, J. Lee J. S. Koros, W. J. Jones, C. W. Nair S., “Facile high-yield solvothermal deposition of inorganic nanostructures on zeolite crystals for mixed matrix membrane fabrication”, *J.*

- Am. Chem. Soc., 131, 14662 (2009).
- [101] Zornoza, B. Téllez, C. Coronas, J., “Mixed matrix membranes comprising glassy polymers and dispersed mesoporous silica spheres for gas separation”, *J. Membr. Sci.*, 368, 100 (2011).
- [102] Anson, M. Marchese, J. Garis, E. Ochoa, N. Pagliero, C., “Abs copolymer-activated carbon mixed matrix membranes for CO₂/CH₄ separation”, *J. Membr. Sci.*, 243, 19 (2004).
- [103] Kim, S. Chen, L. Johnson, J. K., Marand, E., “Polysulfone and functionalized carbon nanotube mixed matrix membranes for gas separation: Theory and experiment”, *J. Membr. Sci.*, 294, 147 (2007).
- [104] Adams, R. Carson, C. Ward, J. Tannenbaum, R. Koros, W., “Metal organic framework mixed matrix membranes for gas separations”, *Microporous Mesoporous Mater.*, 131, 13 (2010).
- [105] Bastani, D. Esmaeili, N. Asadollahi, M., “Polymeric mixed matrix membranes containing zeolites as a filler for gas separation applications: a review”, *J Ind Eng Chem.*, 19, 375 – 93 (2013).
- [106] Bento, A. Lourenco, J. P. Fernandes, A. Ribeiro, MR. Arranz-Andres, J. Lorenzo, V., “Gas permeability properties of decorated MCM-41/polyethylene hybrids prepared by in-situ polymerization”, *J. Membr. Sci.*, 415, 702 (2012).
- [107] Harold, B. Jeazet, T. Staudt, C. Janiak, C., “Metal–organic frameworks in mixed-matrix membranes for gas separation”, *Dalton Trans.*, 41, 14003 (2012).
- [108] Merkel, T. C. Freeman, B. D. Spontak, R. J., He, Z. Pinnau, I. Meakin, P. Hill, A. J., “Ultraporous, reverse-selective nanocomposite membranes”, *Science.*, 296, 519 (2002).
- [109] Ahn, J. Chung, W. J. Pinnau, I. Guiver, M. D., “Polysulfone/silica nanoparticle mixed- matrix membranes for gas separation”, *J. Membr. Sci.*, 314, 123 (2008).
- [110] Reid, B. D. Ruiz-Trevino, A. Musselman, I. H. Balkus, K. J. Ferraris, J. P., “Gas permeability properties of polysulfone membranes containing the mesoporous molecular sieve MCM-41”, *Chem. Mater.*, 13, 2366 (2001).
- [111] Kim, S. Marand, E. Ida, J. Gulians, V.V., “Polysulfone and mesoporous molecular sieve MCM-48 mixed matrix membranes for gas separation”, *Chem. Mater.*, 18, 1149 (2006).
- [112] Kim, S. Marand, E., “High permeability nano-composite membranes based on mesoporous MCM-41 nanoparticles in a polysulfone matrix”, *Microp. Mesop. Mater.*, 114, 129 (2008).
- [113] Vu, D. Q., Koros, W. J., Miller, S. J., “Mixed matrix membranes using carbon molecular sieves. II. Modeling permeation behavior”, *J. Membr. Sci.*, 211, 335 (2003).
- [114] Cong, H. L. Zhang, J. M. Radosz, M. Shen, Y. Q., “Carbon nanotube composite membranes of brominated poly(2,6-diphenyl-1,4-phenylene oxide) for gas separation”, *J. Membr. Sci.*, 294, 178 (2007).
- [115] Kim, S. Chen, L. Johnson, J. K., Marand, E., “Polysulfone and functionalized carbon nanotube mixed matrix membranes for gas separation: Theory and experiment”, *J. Membr. Sci.*, 294, 147 (2007).

- [116] Gorgojo, P. Uriel, S. Tellez, C. Coronas, J., "Development of mixed matrix membranes based on zeolite Nu-6(2) for gas separation", *J. Microporous Mesoporous Mater.*, 115, 85 (2008).
- [117] Liu, Y. Peng, D. He, G. Wang, S. Li, Y. Wu, H. Jiang, Z., "Enhanced CO₂ permeability of membranes by incorporating polyelectrolyte@CNT composite particles into polyimide matrix", *ACS Appl. Mater. Interfaces.*, 6, 13051 (2014).
- [118] Li, Y. Chung, T. S. Huang, Z. Kulprathipanj, a., "Dual-layer polyethersulfone (PES)/BTDA-TDI/MDI co-polyimide (P84) hollow fiber membranes with a submicron PES-zeolite beta mixed matrix dense-selective layer for gas separation", *J. Membr. Sci.*, 277, 28 (2006).
- [119] Aroon, M. A. Ismail. A. F. Matsuura, T. Montazer-Rahmati, M. M., "Performance studies of mixed matrix membranes for gas separation: A review", *Separation and Purification Technology.*, 75, 229 (2010).
- [120] Vu, D. Q. Koros, W. J. Miller, S. J., "Mixed matrix membranes using carbon molecular sieves: I. Preparation and experimental results", *J. Membr. Sci.*, 211, 311 (2003).
- [121] Vu, D. Q., Koros, W. J. Miller, S. J., "Mixed matrix membranes using carbon molecular sieves: II. Modeling permeation behavior", *J. Membr. Sci.*, 211, 335 (2003).
- [122] Jiang, L. Y. Chung, T. S. Cao, C. Huang, Z. Kulprathipanja, S., "Fundamental understanding of nano-sized zeolite distribution in the formation of the mixed matrix single- and dual-layer asymmetric hollow fiber membranes", *J. Membr. Sci.*, 252, 89 (2005).
- [123] Rafizah, W. A. W. Ismail, A. F., "Effect of carbon molecular sieve sizing with poly(vinyl pyrrolidone) K-15 on carbon molecular sieve-polysulfone mixed matrix membrane", *J. Membr. Sci.*, 307, 53 (2008).
- [124] Goh, P. S. Ismail, A. F. Sanip, S. M. Ng, B. C. Aziz, M., "Recent advances of inorganic fillers in mixed matrix membrane for gas separation", *Separation and Purification Technology.*, 81, 243 (2011).
- [125] Moore, T. T., Mahajan, R. Vu, D. Q. Koros, W. J., "Hybrid membrane materials comprising organic polymers with rigid dispersed phases", *AIChE Journal.*, 50(2), 311 (2004).
- [126] Padey, P., Chauhan, R. S., "Membranes for Gas Separation", *Progress in Polymer Science.*, 26, 853 (2001).
- [127] Caro, J. Noack, M., "Zeolite membranes – Recent developments and progress", *Microporous and Mesoporous Materials.*, 115, 215 (2008).
- [128] Hong, M., "Zeolite membranes for hydrogen purification and carbon dioxide removal", Ph.D. Thesis, University of Colorado, 3256383, 2007.
- [129] Xu, X. Bao, Y. Song, C. Yang, W. Liu, J. Lin, L., "Synthesis, characterization and single gas permeation properties of NaA zeolite membrane", *J. Membr. Sci.*, 249, 51 (2005).
- [130] Moore, T. T. Koros, W. J., "Non-ideal effects in organic-inorganic materials for gas separation membranes", *J. Mol. Struct.*, 739, 87 (2005).
- [131] Rodenas, T. van Dalen, M. Garcia-Perez, E. Serra-Crespo, P. Zornoza, B.

- Kapteijn, F. Gascon, J., "Visualizing MOF Mixed Matrix Membranes at the Nanoscale: Towards Structure-Performance Relationships in CO₂/CH₄ Separation Over NH₂-MIL-53(Al)@PI", *Adv. Funct. Mater.* 24, 249 (2014).
- [132] Bae, T. H. Lee, J. S, Qiu, W. L, Koros, W. J. Jones, C. W. Nair, S., "A High-Performance Gas-Separation Membrane Containing Submicrometer-Sized Metal–Organic Framework Crystals", *Angew. CHEM.*, 122, 10059 (2010).
- [133] Robeson, L. M., "The upper bound revisited", *J. Membr. Sci.*, 320, 390 (2008).
- [134] Kim, S. Pechar, T.W. Marand, E., "Poly(imide siloxane) and carbon nanotube mixed matrix membranes for gas separation", *Desalination.*, 192, 330 (2006).
- [135] Kim, S. Chen, L. Johnson, J. K. Marand, E., "Polysulfone and functionalized carbon nanotube mixed matrix membranes for gas separation: Theory and experiment", *J. Membr. Sci.*, 294,147 (2007).
- [136] Aroon, M. A. Ismail, A. F. Montazer-Rahmati, M. M. Matsuura, T., "Effect of Raw Multi-Wall Carbon Nanotubes on Morphology and Separation Properties of Polyimide Membranes", *Separation Science and Technology.*, 45, 2287 (2010).
- [137] Cong, H. Zhang, J. Radosz, M. Shen, Y., "Carbon nanotube composite membranes of brominated poly(2,6-diphenyl-1,4-phenylene oxide) for gas separation ", *J. Membr. Sci.*, 294, 178 (2007).
- [138] Kusworo, T. D. Ismail, A. F. Budiyo, I. N. Widiya, S. Johari, S., "Synthesis and Characterization of Polyimide-Zeolite Mixed Matrix Membrane for Biogas Purification", *International Journal of Engineering Science.*, 1, 1 (2010).
- [139] Jiang, L. Y. Chung, T. Kulprathipanja, S. Chung, N. T. S., "An investigation to revitalize the separation performance of hollow fibers with a thin mixed matrix composite skin for gas separation", *J. Membr. Sci.*, 276, 113 (2006).
- [140] Erickson, K.. Erni, R. Lee, Z. Alem, N. Gannett, W. Zettl, A., "Determination of the local chemical structure of graphene oxide and reduced graphene oxide", *Adv. Mater.*, 22, 4467 (2010).
- [141] Huang , C. Wu, H. Deng, K. Tang, W. Kan, E., "Improved permeability and selectivity in porous graphene for hydrogen purification", *Phys. Chem. Chem. Phys.*, 16, 25755 (2014).
- [142] Tao, Y. Xue, Q. Liu, Z. Shan, M. Ling, C. Wu, T. Li, X., "Tunable Hydrogen Separation in Porous Graphene Membrane: First-Principle and Molecular Dynamic Simulation", *ACS Appl. Mater. Interfaces.*, 6, 8048 (2014).
- [143] Tian ,Z. Mahurin, S. M. Dai, S. Jiang, D. E., "Ion-Gated Gas Separation through Porous Graphene", *Nano Lett.*, 17, 1802 (2017).
- [144] Zhang , Y . Balkus Jr, K. J, Musselman, I. H. Ferraris, J. P., "Metal Organic Framework based Mixed Matrix Membranes: a solution for highly efficient CO₂ capture?", *J. Membr. Sci.*, 325, 28 (2008).
- [145] Chew , T. L. Ahmad, A. L, Bhatia, S., "Ordered Mesoporous Silica (OMS) as an Adsorbent and Membrane for Separation of Carbon Dioxide (CO₂)", *Advances in Colloid and Interface Science.*, 153, 43 (2010).

- [146] Brady, R. Woonton, B. Gee, M. L. O'Connor, A. J., "Investigation of sources and production methods of bioactive peptides effective on human health: A systematic review", *Innovative Food Science & Emerging Technologies*, 9, 243 (2008).
- [147] Shen, Y. Lua, A.Ch., "Preparation and characterization of mixed matrix membranes based on PVDF and three inorganic fillers (fumed nonporous silica, zeolite 4A and mesoporous MCM-41) for gas separation", *Chemical Engineering Journal*, 192, 201 (2012).
- [148] Weng, T. H. Tseng, H. H. Wey, M. Y., "Effect of SBA-15 texture on the gas separation characteristics of SBA-15/polymer multilayer mixed matrix membrane", *J. Membr. Sci.*, 369, 550 (2011).
- [149] Moghadam, F. Omidkhah, M. R, Vasheghani-Farahani, E. Pedram, M. Z. Dorosti F., "The effect of TiO₂ nanoparticles on gas transport properties of Matrimid5218-based mixed matrix membranes. *Separation and Purification Technology*. 77, 128 (2011).
- [150] Mueller, U. Schubert, M. Teich, F. Puetter, H. Schierle-Arndt, K. Pastre, J., "Metal-organic frameworks—prospective industrial applications", *J. Mater. Chem.*, 16, 626 (2006).
- [151] Zornoza, B. Tellez, C. Coronas, J. Gascon, J. Kapteijn, F., "Metal organic framework based mixed matrix membranes: an increasingly important field of research with a large application potential", *Microporous and Mesoporous Materials*. 166, 67 (2013).
- [152] Dybtsev, D. Chun, H. Yoon, S. H. Kim, D. K. "A Simple Metal-Organic Porous Material with High Framework Stability and Highly Selective Gas Sorption Properties", *Journal of the American Chemical Society*, 126, 32 (2004).
- [153] Chen, B. Ockwig, N. W. Millward, A. R. Contreras, D. S. Yaghi, O. M., "High H₂ adsorption in a microporous metal-organic framework with open metal sites", *Angew. Chem. Int. Ed.*, 44, 4745 (2005).
- [154] Wong-Foy, A. G. Matzger, A. J. Yaghi, O. M., "Exceptional H₂ saturation uptake in microporous metal-organic frameworks", *J. Am. Chem. Soc.*, 128, 3494 (2006).
- [155] Furukawa, H. Yaghi, O. M., "Storage of hydrogen, methane, and carbon dioxide in highly porous covalent organic frameworks for clean energy applications", *J. Am. Chem. Soc.*, 131, 8875 (2009).
- [156] Ma, S., Zhou, H. C., "Gas storage in porous metal-organic frameworks for clean energy applications", *Chem. Commun.*, 46, 44 (2010).
- [157] Achmann, S. Hagen, G. mmerle, M. H. Malkowsky I., Kiener C., Moos R., "Sulfur removal from low-sulfur gasoline and diesel fuel by metal-organic frameworks. *Chem. Eng. Technol.* 2010;33:275–280.
- [158] Zacher, D. Shekhah, O. Wo"ll, C. Fischer, R. A., "Thin films of metal-organic frameworks", *Chem. Soc. Rev.*, 38, 1418 (2009).
- [159] Liu, Y. Ng, Z. Khan, E. A. Jeong, H. K. Ching, C. b. Lai, Z., "Synthesis of continuous MOF-5 membranes on porous α -alumina substrates", *Microporous Mesoporous Mater.*, 118, 296 (2009).
- [160] Yoo, Y. Lai, Z. Jeong, H. K., "Fabrication of MOF-5 membranes using

- microwave- induced rapid seeding and solvothermal secondary growth”, *Microporous Mesoporous Mater.*, 123, 100 (2009).
- [161] Zhang, Y. F. Musselman, I. H. Ferraris, J. P. Balkus, Jr. K. J., “Gas permeability properties of Matrimid® membranes containing the metal-organic framework Cu–BPY–HFS”, *J. Membr. Sci.*, 313, 170 (2008).
- [162] Perez, E. V. Balkus, Jr. K. J. Ferraris, J. P. Musselman, I. H., “Mixed- Matrix Membranes Containing MOF-5 for Gas Separations”, *J. Membr. Sci.*, 328, 165 (2009).
- [163] Koros, W. J. Mahajan, R., “Pushing the limits on possibilities for large scale gas separation: which strategies?”, *J. Membr. Sci.*, 175, 181 (2000).
- [164] Zhang, Ch. Dai, Y. Johnson, J. R. Karvan, O. Koros, W. J., “High performance ZIF-8/6FDA-DAM mixed matrix membrane for propylene/propane separations”, *J. Membr. Sci.*, 389, 34 (2012).
- [165] Ordon˜ez, M. J. C. Balkus, Jr. K. J. Ferraris, J. P., “Musselman I. H., Molecular sieving realized with ZIF-8/Matrimid® mixed-matrix membranes”, *J. Membr. Sci.*, 361, 28 (2010).
- [166] Park, K. S. Ni, Z. Coˆte, A. P. Choi, J. Y. Huang, R. Uribe-Romo, F. J. Chae, H. K. O’Keeffe, M. Yaghi, O. M., “Exceptional chemical and thermal stability of zeolitic imidazolate frameworks”, *PNAS.*, 103, 10186 (2006).
- [167] Phan, A. Doonan, Ch. J. Uribe-Romo, F. J. Knobler, C. B. O’Keeffe, M. Yaghi, O. M., “Synthesis, structure, and carbon dioxide capture properties of zeolitic imidazolate frameworks”, *Accounts of Chemical Research.*, 43, 58 - 67 (2010).
- [168] Venna, S. R. Carreon, M. A., “Highly Permeable Zeolite Imidazolate Framework-8 Membranes for CO₂/CH₄ Separation”, *Journal of the American Chemical Society.*, 132, 76 - 78 (2010).
- [169] Park, K. S., Ni, Z., Coˆte, A. P., Choi, J. Y., Huang, R., Uribe-Romo, F. J., Chae, H. K., O’Keeffe, M. and Yaghi, O. M., “The ZIF crystal structures are based on the nets of seven distinct aluminosilicate zeolites: Tetrahedral Si(Al) and the bridging O are replaced with transition metal ion and imidazolate link, respectively”, *PNAS.*, 103 (27), 10186 (2006).
- [170] McCarthy, M. C. Varela-Guerrero, V. Barnett, G. V. Jeong, H. K., “Synthesis of zeolitic imidazolate framework films and membranes with controlled microstructures”, *Langmuir.*, 26, 14636 (2010).
- [171] Li, Y. S. Liang, F. Y. Bux, H. Feldhoff. A. Yang, W. S. Caro, J., “Molecular sieve membrane: supported metal-organic framework with high hydrogen selectivity”, *Angew. Chem. Int. Ed.*, 49, 548 (2010).
- [172] Hung, A. Bux, H. Steinbach, F. Caro, J., “Molecular-Sieve Membrane with Hydrogen Permselectivity: ZIF-22 in LTA Topology Prepared with 3-Aminopropyltriethoxysilane as Covalent Linker”, *Angew. Chem. Int. Ed.*, 49, 4958 (2010).
- [173] Huang, A. S. Dou, W. Caro, J., “Steam-Stable Zeolitic Imidazolate Framework ZIF-90 Membrane with Hydrogen Selectivity through Covalent Functionalization”, *J. Am. Chem. Soc.*, 132, 15562 (2010).
- [174] Bux, H. Chmelik, C. Van Baten, J. M.

- Krishna, R. Caro, J., "Novel MOF-Membrane for Molecular Sieving Predicted by IR-Diffusion Studies and Molecular Modeling", *Adv. Mater.*, 22, 4741 (2010).
- [175] Li, Y. S. Liang, F. Y. Bux, H. G. Yang, W. S. Caro, J., "Zeolitic imidazolate framework ZIF-7 based molecular sieve membrane for hydrogen separation", *J. Membr. Sci.*, 354, 48 (2010).
- [176] Park, K. S. Ni, Z. Côte, A. P. Choi, J. Y. Huang, R. D. Uribe-Romo, F. J. Chae, H. K. O'Keeffe, M. Yaghi, O. M., "Exceptional Chemical and Thermal Stability of Zeolitic Imidazolate Frameworks. *Proc. Nat. Acad. Sci. U.S.A.*, 103, 10186 (2006).
- [177] Ordoñez, M. J. C. Balkus, Jr. K. J., Ferraris, J. P. Musselman, I. H., "Molecular sieving realized with ZIF-8/Matrimid (R) mixed-matrix membranes", *J. Membr. Sci.*, 361, 28 (2010).
- [178] Głowniak, S. Szcześniak, B. Choma, J. Jaroniec, M., "Mechanochemistry: Toward green synthesis of metal-organic frameworks.", 46, 109 (2021).
- [179] Yang, C. Feifei, Z. Yong, W. Chengyin, Y. Jiangfeng, Y. Jinping, L., "Recyclable ammonia uptake of a MIL series of metal-organic frameworks with high structural stability.", 258, 170 (2018).
- [180] Seo, Y. K. J. Yoon, W. Lee, J. S. Hwang, Y. K. Jun, C. H. Chang, J. S. Wuttke, S. Bazin, P. Vimont, A. Daturi, M. Bourrelly, S. Llewellyn, P. L. Horcajada, P. Serre, C. Férey, G., "Energy-Efficient Dehumidification over Hierarchically Porous Metal-Organic Frameworks as Advanced Water Adsorbents", *Adv. Mater.* 24, 806 (2012).
- [181] Horcajada, P. Chalati, T. Serre, C. Gillet, B. Sebrie, C. Baati, T. Eubank, J. F. Heurtaux, D. Clayette, P. Kreuz, C. Chang, J. S. Hwang, Y. K. Marsaud, V. Bories, P. N. Cynober, L. Gil, S. Férey, G. Couvreur, P. Gref, R., "Porous metal-organic-framework nanoscale carriers as a potential platform for drug delivery and imaging", *Nat. Mater.* 9, 172 (2009).
- [182] Horcajada, P., Chevreau, H., Heurtaux, D., Benyettou, F., Salles, F., Devic, T., Garcia-Marquez, A., Yu, C., Lavrard, H., Dutson, C. L., Magnier, E., Maurin, G., Elkaïm, E. and Serre, C., "Extended and functionalized porous iron(III) tri- or dicarboxylates with MIL-100/101 topologies", *Chem. Commun.*, 50, 6872 (2014).
- [183] Leus, K. Bogaerts, T., De Decker, J. Depauw, H. Hendrickx, K. Vrielinck, H. Van Speybroeck, V. Van Der Voort, P., "Systematic study of the chemical and hydrothermal stability of selected "stable" Metal Organic Frameworks", *Microporous Mesoporous Mater.*, 226, 110 (2016).
- [184] Fang, Y., Wen, J., Zeng, G., Jia, F., Zhang, S., Peng, Z. and Zhang, H., "Effect of mineralizing agents on the adsorption performance of metal-organic framework MIL-100(Fe) towards chromium(VI)", *Chem. Eng. J.*, 337, 532 (2018).
- [185] Seo, Y. K. Yoon, J. W. Lee, J. S. Lee, U. H. Hwang, Y. K. Jun, C. H. Horcajada, P. Serre, C. Chang, J. S., "Large scale fluorine-free synthesis of hierarchically porous iron(III) trimesate MIL-100(Fe) with a zeolite MTN topology", *Microporous Mesoporous Mater.*, 157, 137 (2012).
- [186] Zou, D. Liu, D., "Understanding the modifications and applications of highly

- stable porous frameworks via UiO-66”, *Materials today chem.*, 12, 139 (2019).
- [187] UiO-66 Zirconium Building Bricks for Stable Metal Organic Frameworks, Strem: Catalog No. 40-1105, Zirconium 1,4-dic
- [188] Li, J. R Kuppler, R. J. Zhou, H. C., “ Selective gas adsorption and separation in metal–organic frameworks”, *Chem. Soc. Rev.*, 38, 1477 (2009).
- [189] Keskin, S. van Heest, T. M. Sholl, D. S., “ Can Metal–Organic Framework Materials Play a Useful Role in Large-Scale Carbon Dioxide Separations?”, *ChemSusChem.*, 3, 879 (2010).
- [190] Duren, T. Bae, Y. S. Snurr, R. Q., “ Using molecular simulation to characterise metal–organic frameworks for adsorption applications”, *Chem. Soc. Rev.*, 38, 1237 (2009).
- [191] Calero , S. Martin-Calvo, A. Hamad, S. Garcia-Perez, E., “ On the performance of Cu-BTC metal organic framework for carbon tetrachloride gas removal”, *Chem. Commun.*, 47, 508 (2011).
- [192] Castillo, J. M. Vlugt, T. J. H. Calero, S., “Understanding Water Adsorption in Cu–BTC Metal–Organic Frameworks”, *J. Phys. Chem. C.*, 112, 15934 (2008).
- [193] Martin-Calvo, A. Garcia-Perez, E. Castillo, J. M. Calero, S., “ Molecular simulations for adsorption and separation of natural gas in IRMOF-1 and Cu-BTC metal-organic frameworks”, *Phys. Chem. Chem. Phys.*, 10, 7085 (2008).
- [194] Chui, S. S. Y. Lo, S. M. F. Charmant, J. P. H. Orpen, A. G. Williams, I. D., “A Chemically Functionalizable Nanoporous Material [Cu₃(TMA)₂(H₂O)₃]_n”, *Science.*, 283, 1148 (1999).
- [195] Krishna, R. van Baten, J. A., ”Investigating Cluster Formation in Adsorption of CO₂, CH₄, and Ar in Zeolites and Metal Organic Frameworks at Subcritical Temperatures”, *Langmuir.*, 26, 3981 (2010).
- [196] Garcia-Perez, E. Gascon, J. Morales-Florez, V. Castillo, J. M., Kapteijn, F. Calero, S., “Identification of Adsorption Sites in Cu-BTC by Experimentation and Molecular Simulation”, *Langmuir.*, 25, 1725 (2009).
- [197] Babarao , R. Jiang, J. W., “Diffusion and Separation of CO₂ and CH₄ in Silicalite, C168 Schwarzite, and IRMOF-1: A Comparative Study from Molecular Dynamics Simulation”, *Langmuir.*, 24, 5474 (2008).
- [198] Babarao, R. Jiang, J. W. Sandler, S. I., “Molecular Simulations for Adsorptive Separation of CO₂/CH₄ Mixture in Metal-Exposed, Catenated, and Charged Metal–Organic Frameworks”, *Langmuir.*, 25, 5239 (2009).
- [199] Keskin, S. Liu, J. C. Johnson , J. K. Sholl, D. S., “Atomically detailed models of gas mixture diffusion through CuBTC membranes”, *Microporous Mesoporous Mater.*, 125, 101 (2009).