RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

RSC Advances

RSCPublishing

REVIEW ARTICLE

An Overview: Synthesis of thin films/membranes of Metal Organic Frameworks and its gas separation performances

Cite this: DOI: 10.1039/x0xx00000x

Zee Ying Yeo[a], Siang-Piao Chai[a]*, Peng Wei Zhu[b], Abdul Rahman Mohamed[c]

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Metal organic frameworks (MOFs), an emerging class of porous solid materials have developed into a constructive research field with their intense research interests mainly in the field of materials science and chemistry. Being in their early stage of development, the research progress in MOFs membranes has exhibited promising results despite several challenges associated with its fabrications. In this review, we introduced the methods in fabrication of MOF membranes (*in-situ* and secondary growth), challenges associated with MOFs membranes fabrication such as poor interaction with its substrates, moisture instability and easily induced macroscopic cracks followed by strategies of researchers adopted in overcoming these difficulties. At the same time, the gas separation performances of these MOFs membranes were discussed and compared.

1. Introduction

In the past two decades, synthesis of metal organic frameworks (MOFs) has attracted tremendous attention due to its plausible potential to obtain exceptionally interesting structures for applications in various fields related to porous materials. This includes carbon capture and storage [1-5], separation applications [6-11], and catalysis [12-17], depending on the pore size and shape as well as host guest interactions involved [18]. Several excellent reviews published on MOFs could be found in these literatures [19-25]. Membrane gas separation is principally based on the differences in the diffusion rates of gas molecules within the membrane materials, where its separation performance was determined by sizes of the gas molecules and microstructure of the membrane. The separation performance of a membrane is usually described by both permeability and selectivity. The permeability approximate the transport rate of species through the membrane, while selectivity assess the capability of the membrane to separate components of a mixture.

Membrane based separations offer great potential in terms of their energy efficiency, resulting in less investment costs as compared to other competing technologies such as pressure swing adsorption and cryogenic distillation [26]. The current market for membrane gas separation largely depends on polymeric membranes due to the fact that they have distinct advantages such as low production costs and high permeation fluxes [27, 28]. Permeation technologies based on conventional polymeric membranes have also been developed in the industry, etc. nitrogen production and hydrogen recovery [29]. Nonetheless, the inherited challenges of polymeric membrane have generally limit them to the separation of non-condensable gases (etc. CO_2/CH_4, H_2/N_2), where the harsh operating conditions to which these polymeric membranes will be exposed often result in plasticization effect [30]. On the other hand, zeolite molecular sieve have been investigated in terms of their application in membrane separations due to their well-defined regular pore structure with high thermal and chemical stability. The uniform pore size determined by their crystallographic structure makes zeolite membranes attractive to achieve high selectivity due to molecular sieving effect. Regardless of these advantages, inorganic membranes have not found major industrial applications in gas separation except the de-watering of bio-ethanol by steam permeation using supported zeolite LTA (Linde-type-A) membranes [31]. Apart from its high production costs, formation of non structural pores in real zeolite membranes is another issue that leads to difficulties in scaling up [30, 31]. Nonetheless, these zeolite membranes continue to attract a great deal of attentions due to their excellent separations performance. Several zeolite membranes (etc. DDR, T-type) have demonstrated very high CO_2/CH_4 selectivity as observed in selected publications [32-34]. Mixed matrix membranes with porous or non porous fillers deposited into polymeric membrane could enhance the permeability and selectivity of polymeric membrane. These hybrid membranes could combine the advantages of both phases: the superior gas transport properties of molecular sieves (high selectivity of the filler phase) with desirable mechanical properties, together with low cost and good processability of the base polymers [35, 36]. Although mixed matrix membrane has shown to be successful and promising [37-40], the main challenges often encountered is the void spaces between the inorganic filler (etc. zeolites) and the polymer base which allow gas molecules to channel through, resulting in a deteriorated selectivity. However, with MOFs (metal ions/clusters and organic ligands) appear as inorganic-organic

solids, they are expected to demonstrate better compatibility with polymers, due to better affinity of the MOF linkers with the polymer chains, resulting in mixed matrix membranes with lower degree of defects [37, 41]. For instance, Sorribas et al. [42] prepared mixed matrix membranes comprising of silica-ZIF-8 core shell spheres in polysulfone matrix for CO_2 and CH_4 separation. In addition, Hsieh et al. [43] synthesized "breathing" MIL-53 into Matrimid® forming mixed matrix membranes. Interestingly, they found that the reversibly changing of open-pore to closed-pore framework (breathing effect) of the MIL-53 was stabilized when embedded into the polymer matrix, suggesting the breathing framework can be controlled with the restrictive effect in the polymer matrix.

Despite the devoted efforts and research progress made with different materials as membranes for gas separation, challenges such as inadequate selectivity and low permeability remain to be overcome. MOF, distinguished by their high potential for specific functionalization allowing the tuning of adsorptive interaction and the control of pore size *via* functional groups, makes them an exciting candidate for gas separation as membrane materials [44, 45]. Obviously, membranes fabricated by materials with uniform pore sizes are much more preferable due to the pore size distribution which plays a crucial role in separation performance. Despite researching for many years, applications of zeolite membranes are still impeded by a limited choice of structure types (pore sizes) and difficulty in scaling up due to formation of defects. MOFs, similar to zeolites, possesses properties such as well defined pore size and shape that seemed promising for advanced membranes. In the context of this review, we will discuss the continuous film of MOFs membranes, significant advances on the fabrication methods on these membranes as well as their gas transport properties.

2. Fabrication of MOF membranes via *in-situ* and secondary growth

Continuous and well inter-grown MOF membranes are potential candidates for practical gas separation applications. Several techniques have been described in the literature to synthesize MOF membranes, they generally are *in-situ* synthesis and secondary (seeded) growth. There are several other techniques that have been reported for the synthesis of MOFs thin films, including self assembled monolayers (SAMS) [46-48], layer by layer deposition [49-52], colloidal deposition approach [53], and electrochemical deposition of MOF-films [54-57]. The attention of interested readers in these MOF thin films synthesis could be directed to these articles [24, 46-60].

In-situ involves only one step synthesis to fabricate membranes, but does not offer the microstructure control and substrate independence of secondary (seeded) growth. This technique rely on the direct immersion of supports in precursor solutions containing both metal salts and linkers. Implementation of conventional or microwave heating will generate nucleation sites on the supports, leading to growth of crystals on the substrate. This method has been observed to be difficult in preparation of continuous films on bare substrates due to poor heterogeneous nucleation. Therefore, some researchers has reported chemical modifications on the supports in order to obtain high quality MOF membranes. The most important step of secondary (seeded) growth is the seed crystals attachment to the support followed by immersion of the seeded support in the precursor solution of the particular MOF, where membranes are produced in a procedure similar to *in-situ* growth. With the existence of nuclei on the support surface, the influence of the support's surface chemistry are mostly eliminated. In many cases, secondary growth are preferably adopted to prepare membranes, since the drawback of *in-situ* growth will lead to poor coverage of crystallites on bare substrates.

2.1. *In-situ* synthesis

In-situ synthesis of MOFs membranes could be further branched into non-modified and modified substrates. Surface modified substrate for the synthesis of MOFs membranes are further discussed and elaborated in section 3.1. On the other hand, only several MOFs membranes have demonstrated *in-situ* growth using non-modified substrates [61-63]. ZIF-8, under the family of ZIFs, possesses high chemical and thermal stability with sodalite-type structure of narrow pore aperture of 0.34 nm, is thus highly attractive for membrane based applications. For instance, Bux et al. [61] employed titania disc support for the preparation of ZIF-8 membrane with thickness of ~30nm, achieving H_2/CH_4 selectivity of 11.2 thereby proving the ZIF-8 membrane fabricated was dense and crack free.

Another popular MOF, named MOF-5, was prepared by Liu et al. [63] on porous α-alumina substrate *via in-situ* synthesis. The permeation data for H_2, CH_4, N_2, CO_2, and SF_6 gases exhibited gas transport behaviour consistent with a Knudsen type diffusion mechanism. This gas transport behaviour observed was specifically derived from the structural features of the framework with their MOF-5 pore size distribution centred around 1.56 nm. Here, their large channel dimensions within MOF-5 membrane was postulated to lead to lower contributions of gas molecules collisions with the pore walls, resulting in Knudsen behaviour mechanism. However, it is also important to note that inter-crystalline boundary defects will contribute significantly to the overall transport mechanism *via* diffusion of the gas molecules, though such macroscopic defects were not observed under their scanning electron microscopy images.

Furthermore, Cao et al. [64] prepared Cu-BTC membrane on novel potassium hexatitanate ($K_2Ti_6O_{13}$) support where this support can adsorb Cu^{2+} in a moderate acid environment which is more suitable for growth of Cu^{2+} containing MOF membranes. The supports were treated in KOH solution to increase the concentration of free hydroxyl groups on the support's surface leading to more connection nodes for Cu-BTC growth. The Cu-BTC membrane displayed He/CO_2

selectivity of 3.4 with He permeance of 1.4 x 10^{-6} mol/m^2.s.Pa.

The adherence of both MOF layer and substrate plays an important role for the growth of MOFs membranes. It is generally easier for the growth of MOFs on polymer surface as their organic linkers have higher affinity towards the polymer surface. For example, Ben et al. [65] prepared a free standing HKUST-1 membrane for gas separations, initially utilizing a polymer substrate. As shown in **Figure 1**, their procedure involves spin coating of PMMA(poly(methyl-methacrylate)) onto a silica wafer followed by reaction with sulfuric acid to hydrolyze the external PMMA into PMAA(poly(methacrylic-acid)). Then, the PMMA-PMAA-silica substrate was introduced into the HKUST-1 precursor at 120°C for 3 days for membrane formation. Further immersion of the resultant membrane in chloroform could dissolve the PMMA-PMAA thin film and rendered the HKUST-1 membrane to be free standing. Their H_2/N_2, H_2/CH_4, and H_2/CO_2 equimolar gas permeation achieved separation factor of 8.9, 11.2, and 9.3, respectively, at 25°C and 1 bar.

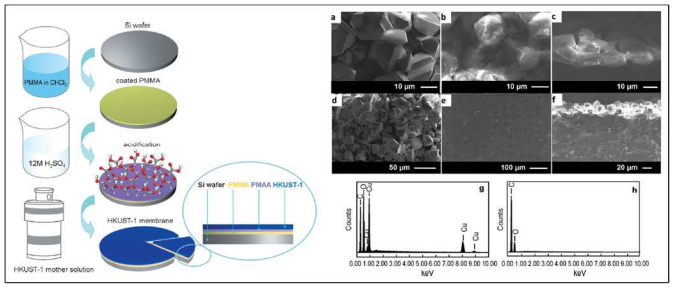

Fig 1. Left side: Schematic illustration of the preparation of free standing HKUST-1 membrane. Right side: SEM images of the free-standing HKUST-1 microporous membrane: a) top surface, b) bottom surface, c) cross-section; and SEM images of the PMMA-PMAA-supported HKUST-1 microporous membrane: d) top surface, e) bottom surface, and f) cross-section. EDS of a cross-section of PMMA–PMAA-supported HKUST-1 membrane: (g) MOF layer and (h) polymer layer.

Consequently, Yao et al. [62] developed a contra-diffusion method to prepare ZIF-8 films on both sides of a nylon substrate separating both zinc nitrate and 2-methylimidazole solutions where crystallization occurs on the membrane surfaces through solution contra-diffusion, shown in **Figure 2**. Continuous film of ZIF-8 was successfully fabricated on the zinc nitrate side of the nylon substrate with thickness up to ~16μm. Their sample exhibited H_2/N_2 selectivity of ~4.3 with H_2 permeance of 1.97 x 10^{-6} mol/m^2.s.Pa which further confirmed the ZIF-8 films were continuous and compact. On the other hand, Hara et al. [66] demonstrated inter-crystalline defects can be reduced by applying counter diffusion method for the preparation of Cu-BTC membrane. Based on the concept of reactant solutions supplied from the opposing sides of the support, reaction will occur within the pores until the MOF layer is "plugged" which eliminates inter-crystalline defects. Their Cu-BTC membrane shows an increased H_2 selectivity and lower permeance with increasing preparation times, leading to ideal H_2/CH_4 selectivity of 153. Recently, the same group of researchers [67] synthesized ZIF-8 by applying counter diffusion method, displayed ideal separation factors for H_2/C_3H_8 and C_3H_6/C_3H_8 of 2000 and 59, respectively, with H_2 and C_3H_6 permeances of 9.1 x 10^{-8} and 2.5 x 10^{-9} mol/m^2.s.Pa, respectively. The huge separation factor of H_2/C_3H_8 clearly evidenced the potential separation ability of ZIF-8.

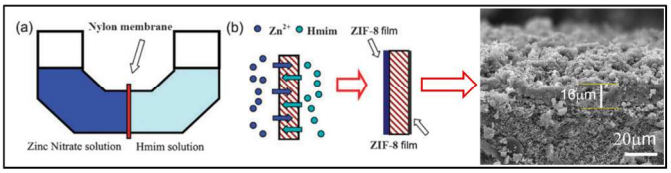

Fig 2. (a) Diffusion cell for ZIF-8 film preparation and (b) the schematic illustration of ZIF-8 films preparation on both sides of the nylon support *via* contra-diffusion of Zn^{2+} and 2-methyl-imidazole through the pores of the nylon support (Left). SEM image of the cross-section ZIF-8 film prepared at room temperature for 72 h at the zinc nitrate solution side (Right).[62]

Interestingly, Shah et al. [68] developed a new synthesis protocol called "rapid thermal deposition (RTD)" based on the concept of evaporation-induced crystallization performed at elevated temperature. In this method, α-alumina porous supports are initially soaked with MOF precursor solution and subjected to 180°C, where solvent evaporation will drive the flow of the precursor solution from inside the supports to outside where crystallization occurs. RTD was applied to both HKUST-1 and ZIF-8 membranes. The prepared HKUST-1 membranes showed very high (~600) H_2/SF_6 ideal selectivity whereas ZIF-8 membranes exhibited an average C_3H_6/C_3H_8 selectivity of ~30.

2.2. Secondary (Seeded) growth

Despite several new strategies have been employed to deposit seed layer on the substrate prior to secondary growth, Venna et al. [69] synthesized ZIF-8 membranes by conventional rubbing seeding on tubular α-alumina supports. Their ZIF-8 membranes (~5-9μm thickness) exhibited unprecedented CO_2 permeances of ~2.4 x 10^{-5} mol/m^2.s.Pa with CO_2/CH_4 selectivies in the range of 4-7. It was unexpected to see the ZIF-8 membrane displayed a moderate selectivity for CO_2 over CH_4 despite the pore diameter of ZIF-8 (0.34 nm) falls in between the kinetic diameter of CO_2 (0.33 nm) and CH_4 (0.38 nm). In spite of the fact that the pore window of ZIF-8 is estimated to be 0.34 nm from crystallographic data, however, several literatures [70-72] have reported that the ZIF-8 framework structure is in fact more flexible and even large molecules like CH_4 (critical diameter of 0.38 nm) can easily permeate through the pore network. In line with their moderate selectivity, it is important that high CO_2 selectivity at this stage of MOFs research could be achieved for any potential industrial applicability.

Nan et. al. [73] applied a step-by-step seeding procedure to obtain a uniform seed layer on the alumina support, followed by secondary growth to formation of HKUST-1 membrane. The single gas permeation of the step-by-step HKUST-1 membranes has resulted in ideal selectivities of 2.9, 3.7, and 5.1 for H_2/CH_4, H_2/N_2, and H_2/CO_2, respectively, approaching

the corresponding Knudsen selectivities. Initially *in-situ* hydrothermal growth experiment for the formation of HKUST-1 membrane has been constructed, however, the discontinuous HKUST-1 membranes indicated that HKUST-1 crystals were prone to grow in the solution rather than on the bare support.

On the other hand, reactive seeding involves bonding the membrane support with its required precursor to form the seed layer for further secondary hydrothermal synthesis of MOFs membranes synthesis. It can also be carried out using *in-situ* growth to generate seeds on the substrate. As reported by Hu et al. [74], preparation of MIL-53 membrane on alumina support was performed (**Figure 3**). In the procedure, α-alumina support was seeded with 1,4-benzenedicarboxylic acid (H_2BDC) under mild hydrothermal method (Figure 3a), followed by secondary growth with precursor containing both $Al(NO_3)_3{\cdot}9H_2O$ and H_2BDC. Figure 3c and 3d show the surface of highly intergrowth MIL-53 membrane synthesized and cross sectional area of well bonded MIL-53 membrane on the support, respectively. In a similar manner, Nan et al. [75] also developed reactive seeding method for the synthesis of MIL-53 and MIL-96 membranes. They investigated the interactions between the support and organic precursor where a two-step mechanism of reactive seeding method was proposed. Based on the mechanism, the alpha alumina support was initially reacted with H_2O at 210°C to produce γ-AlO(OH), then with γ-AlO(OH) interacted with H_3(btc) to form MIL-96 seeds.

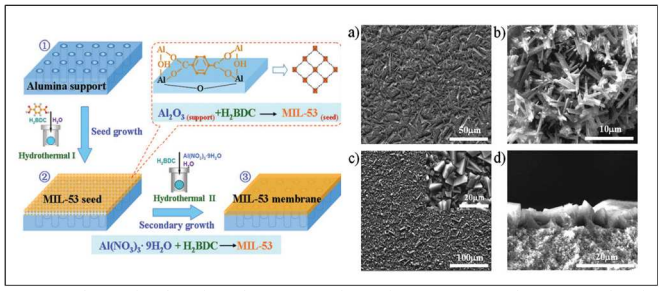

Fig 3. Schematic showing the preparation of MIL-53 membrane on alumina support *via* the reactive seeding method (Left). SEM images of (a) MIL-53 seed layer (b), MIL-53 powders, (c) MIL-53 membrane surface and (d) cross-section (Right). [74]

Here, a counter diffusion method involving seeding process has been demonstrated by Kwon et al. [76] for the synthesis of ZIF-8 membrane, shown in **Figure 4**, where the porous α-alumina support is soaked in a metal precursor followed by rapid solvothermal reaction in a ligand solution. During the reaction, the concentration gradients facilitate metal ions and ligands to diffuse from the support into the solution and vice versa. The authors claimed that their shorter reaction time method is better than the typical counter-diffusion which involves longer diffusion rates, where they revealed ZIF-8 membrane thickness of only 1.5μm. It is inspiring that their propylene/propane (C_3H_6/C_3H_8) separation of ZIF-8 demonstrated an excellent separation factor of ~55 even only synthesized for 30 minutes. The author concluded that the counter diffusion method enabled the defective membranes to be identified and healed without disassembling the membrane modules.

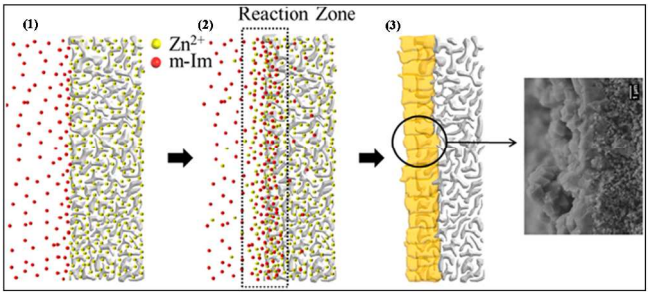

Fig 4. Schematic illustration of ZIF-8 membrane synthesized *via* counter-diffusion method: (1) porous alumina support saturated with metal precursor solution (Zn^{2+}) placed in a ligand solution (m-Im) containing sodium formate; (2) diffusion of metal ions and ligand molecules causing the formation of a "reaction zone" at the interface; and (3) rapid heterogeneous nucleation/crystal growth at the interface leads to well inter-grown ZIF-8 membrane.[76]

3. Challenges associated with MOFs membranes Fabrication

Successful synthesis of MOFs with sufficient quality for gas separation remain as a challenging task due to the inherent weak coordination bonds of MOFs and its unfavourable heterogeneous nucleation. These weak properties of MOFs has called for more research efforts in order to successfully synthesize better quality MOFs membranes. With MOFs emerging as a new nanoporous material, expectations arise on whether MOFs could overcome all the challenges and barriers characterized by other membrane materials. The general challenges associated with fabrication of MOFs membranes generally include (1) poor interaction with substrate, (2) moisture instability (water replacing carboxylates), (3) easily induced macroscopic cracks. Although these challenges represent a common difficulty in MOFs membrane fabrication, they do not say the same for all kinds of MOFs membranes.

3.1. Poor interaction of MOFs with substrate

Several MOFs such as MOF-5 [77] have been reported to have insufficient interfacial interaction with substrates for synthesis of MOFs membranes [77-83]. Researchers have reported various techniques to improve the MOFs crystals adhesion to the membrane support for membrane fabrication. They include support modification with chemicals to enhance the covalent linking between MOFs and support, the use of polymer binders and graphite coatings to improve the secondary binding *via* hydrogen bonding, or by having pre-attached seed crystals to the support so that crystallization growth will be more substrate independent.

For instance, Xie et al. [81] deposited APTES functionalized α-Al_2O_3 particles onto coarse macroporous support for the formation of ZIF-8 membrane. Apart from pore structure modification of the coarse macroporous support, the APTES modified α-Al_2O_3 served to promote high density of

heterogeneous nucleation sites to produce thin and defect free ZIF-8 membrane. Inspired by Huang et al, [80, 84] APTES grafted on TiO_2 or Al_2O_3 support can promote heterogeneous nucleation of ZIF-22 (pore size of 0.30 nm) and ZIF-90 (pore size of 0.35 nm) to form dense membranes. As evaluated in gas permeation experiments, ZIF-8 membrane of Xie et al. [81] exhibited remarkably high H_2 permeance of $5.73x10^5$ mol/m^2.s.Pa with H_2/N_2 and H_2/CO_2 selectivity of 15.4 and 17.0, respectively. Simultaneously, Huang et al. [80] reasoned that the 3-aminopropylsilyl groups of APTES can coordinate to the free Zn^{2+} centers and bind the growing nanocrystals forming covalent linker between the growing ZIF-22 layer and the support. The ideal separation performance of ZIF-22, determined by the ratio of single component permeances, displayed H_2/CO_2, H_2/O_2, H_2/N_2, and H_2/CH_4 selectivity of 8.5, 7.2, 7.1, and 6.7, respectively. In addition, the binary separation of H_2/CO_2, H_2/O_2, H_2/N_2, and H_2/CH_4 also displayed selectivity of 7.2, 6.4, 6.4 and 5.2, respectively, which exceed the corresponding Knudsen constants.

Also, in a recent paper reported by Huang et al. [85], they progress to prepare a highly permselective ZIF-8 membrane supported on polydopamine (PDA) functionalized stainless steel nets (SSN). The high void volume of the SSN with thread woven of 25 μm thick and aperture of 30 × 30 μm is expected to boost the gas permeances through the membrane. With similar ideology, they promote the nucleation and growth of well inter-grown ZIF-8 membranes on SSN by functionalization with PDA due to its strong adhesive ability *via* formation of strong non covalent and covalent bonds with surface hydroxy groups. The schematic diagram for preparation of PDA modified SSN supported ZIF-8 layer was shown in **Figure 5**. Attributing to the adhesive ability of PDA, well inter-grown and highly selective ZIF-8 membrane was prepared and strongly anchored to the SSN support (Figure 5c,d) as compared to the poorly inter-grown ZIF-8 layer with obvious intercrystalline gaps as observed in non-modified SSM (Figure 5a,b). Their binary separation at 100°C and 1 bar demonstrated H_2/CO_2, H_2/N_2, H_2/CH_4 and H_2/C_3H_8 separation factors of 8.1, 15.0, 23.2 and 329.7, respectively, far beyond Knudsen coefficients. Their displayed H_2 permeance > 2.1 x 10^{-5} mol/m^2.s.Pa is by far the highest H_2 permeance in ZIF-8 membranes up to date. These results demonstrated the ZIF-8 capabilities of separating H_2 from other gases, especially C_3H_8.

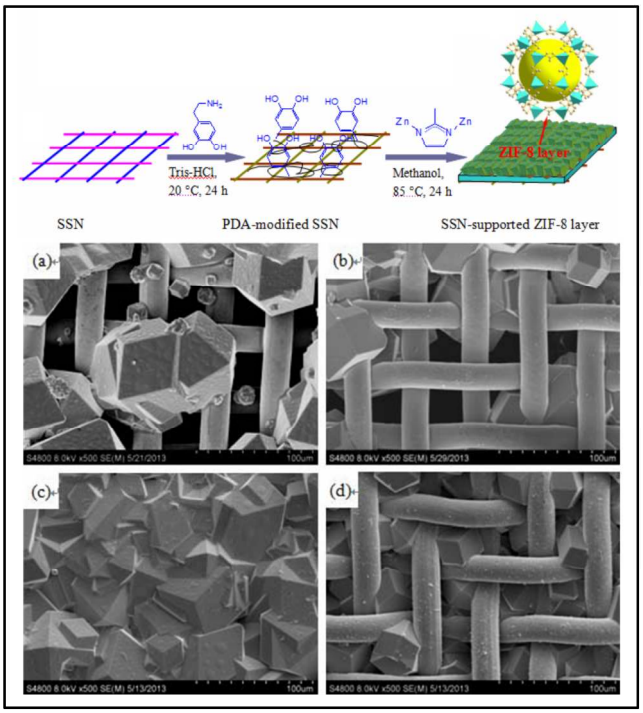

Fig 5. Schematic illustration of the ZIF-8 membrane preparation on PDA-functionalized SSN (Top). FESEM images of upper side (a) and down side (b) of the ZIF-8 layer prepared for 24 h on non-modified SSN, FESEM images of upper side (c) and down side (d) of the of ZIF-8 membrane prepared for 24 h on PDA-functionalized SSN (Bottom). [85]

Guo et al. [86] introduced the "twin copper source" growth method for the preparation of $Cu_3(BTC)_2$ membrane. A copper net support of 400 mesh was oxidised followed by placing into the reaction solution for $Cu_3(BTC)_2$ film growth in a teflon-lined autoclave. By oxidizing the copper net before the hydrothermal synthesis, homogeneous nucleation sites are formed for the continuous film growth. The ions of Cu^{2+} both on the copper net and in the reaction solution acted as metal source for crystal growth. Subjected to gas permeation tests, their $Cu_3(BTC)_2$ membrane displayed binary separation factor of 7.04, 6.84, and 5.92 for H_2/N_2, H_2/CO_2, and H_2/CH_4, respectively with H_2 permeance of $1.07x10^{-1}$ mol/m^2.s.Pa; and ideal separation factor of 4.60, 4.52, and 7.8 for H_2/N_2, H_2/CO_2, and H_2/CH_4, respectively with H_2 permeance of $1.27x10^{-1}$ mol/m^2.s.Pa. This separation performance is far beyond the Knudsen diffusion behaviour, with H_2 permeance higher than other gases indicating this membrane has a high preference for the selectivity of H_2. Besides, the binary separation factors of H_2/N_2 and H_2/CO_2 are both higher than its ideal separation factor while H_2/CH_4 ideal separation factor is higher than its binary separation factor. This could be due to the slower diffusing CH_4 with stronger sorption will prohibit the diffusion of faster diffusing H_2 in the mixture. Though it sounds interesting for the copper net to represent both as physical supports as well as copper source for the membrane crystallization, its inherent free standing characteristics may induce mechanical stability in long term practical applications.

Thermal seeding technique, by introducing the seed crystals together with both organic ligands and species in the seed suspensions for seeding at elevated temperature, was found to be an interesting approach to strongly bound the seed crystals to the porous supports. Guerrero et al. [79] reported the fabrication of a continuous HKUST-1 membranes *via* thermal seeding technique. It was hypothesized that the un-reacted ligands and Cu complex serve as binders for the binding between the HKUST-1 seed crystals and alumina support [79]. The maximum ideal selectivity of the HKUST-1 membrane attained H_2/N_2, H_2/CH_4 and H_2/CO_2 selectivities of 7.5, 5.7, and 5.1, respectively. On the other hand, McCarthy et. al [78] employed a support modification process for the synthesis of ZIF-8 membrane. Similar to the thermal seeding technique reported by Guerrero et al. [79], yet, the significant difference is the usage of organic linker solution instead of the seed crystals solution. They observed that solvothermal synthesis without surface modification of the support does not produce ZIF-8 films. Firstly, this phenomena indicated that heterogeneous nucleation is not favoured on unmodified α-alumina due to lack of interaction between ZIF-8 and porous α-alumina support. Secondly, the high temperature surface modification process was expected to ensure linkers are attached to the support surface *via* an activated process which forms covalent bonding of Al-N. Their ZIF-8 membrane exhibited molecular sieving behaviour with ideal selectivities of 11.6 and 13 for H_2/N_2 and H_2/CH_4, respectively.

Since continuous films are difficult to be formed directly on bare alumina supports, anchoring seed crystals to the surface of the support by treatment of the substrate with polyethyleneimine coating or chitosan binder has been recommended. Ranjan et al. [87] synthesized MMOF membranes *via* seeded growth on a surface modified α-alumina support. The α-alumina support was modified using polyethyleneimine (PEI) for enhanced attachment of seeds *via* hydrogen bonding. The membrane exhibits a moderate selectivity of H_2/N_2 and H_2/CO_2 both around ~4.0 at room temperature. However, increasing the temperature to around 190°C, the ideal selectivity of H_2/N_2 reaches to ~23. Li et al. [88] also performed secondary seeded growth in synthesizing ZIF-7 membrane using PEI as a binder, shown in **Figure 6**. It could be clearly seen in Figure 6b,c that ZIF-7 layer was deposited on the support with thickness of just ~1.5 µm, representing one of the thinnest MOFs based membrane reported up to date. PEI was expected not only to stabilize the seed particles in the suspension but also to enhance the linkage between the seeds and the support through hydrogen bonding interactions. ZIF-7 membrane exhibits a pore diameter of approximately 0.3 nm, achieving H_2/CO_2 ideal selectivity and separation factor of 6.7 and 6.5, respectively; while for 1:1 binary mixtures, their H_2/N_2 and H_2/CH_4 separation factors was found to be 7.7 and 5.9, respectively (at 200°C and 1 bar). On the similar manner, Zhou et al. [89] used chitosan as a binder to improve the binding force between $Cu_3(BTC)_2$ seeds and hollow ceramic fiber (HCF) porous support due to its abundance in amino and hydroxyl groups. The chitosan played a key role in strengthening the mutual interaction between the support and $Cu_3(BTC)_2$ crystals in preparation of the membrane. The as-prepared membrane shows high H_2 single gas permeance of $7.25x10^{-8}$ mol/m^2.s.Pa and binary permeances in the range of 3.23 - $4.10x10^{-8}$ mol/m^2.s.Pa. At the same time, their membrane shows separation factors of 8.66, 13.56, and 6.19 for H_2/N_2, H_2/CO_2, and H_2/CH_4 gas mixtures, respectively.

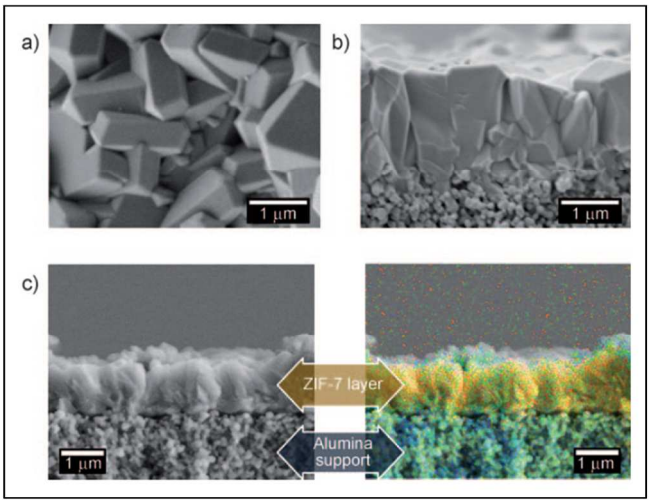

Fig 6. (a) surface and (b) cross section SEM images of ZIF-7 membrane. (c) cross section SEM image of the ZIF-7 membrane (left) and the same image overlaid with an EDX mapping (right). In the EDX mapping, light orange and cyan represent Zn and Ti, respectively, the results clearly show the clean formation of the ZIF-7 layer on the alumina support. [88]

Coatings of membrane substrates could also be performed in order to enhance the overall formation of the MOFs membranes. Yoo et al. [90] reported a microwave induced thermal deposition method to prepare MOF-5 crystals on different porous substrates. MOF-5 were grown on three different substrates (bare anodized Al_2O_3, carbon coated Al_2O_3, and graphite coated Al_2O_3) prepared under 30 seconds of microwave irradiation. The kinetics of heterogeneous nucleation and growth of MOF-5 crystals are enhanced when thin conductive layers such as carbon or graphite are coated as compared to bare substrates. Upon close examination of the morphology of the film, graphite coated MOF-5 membrane shows more densely packed MOF-5 crystals as compared to carbon coated and bare substrate membrane. The smaller size and higher density of MOF-5 crystals formation on the graphite coated substrate was explained by rapid formation of more nuclei on the graphite surface under microwaves, followed by their mass transfer limited growth.

H. K. Jeong's group [78] has initially prepared ZIF-8 membrane through *in-situ* synthesis using 2-methylimidazole modified support with the resulted 20 µm membrane thickness exhibiting H_2 permeance of ~$1.8x10^{-7}$ mol/m^2.s.Pa. Furthermore, they have innovated new methods to prepare ZIF-8 membranes which include rapid thermal deposition [68] and *in-situ* counter diffusion method [76]. The rapid thermal deposition preparation method resulted in 5-20 µm membrane thickness with highest propylene binary permeance of $8.1x10^{-9}$ mol/m^2.s.Pa with propylene/propane binary selectivity of 41.

On the other hand, the *in-situ* counter diffusion method has produced ZIF-8 membrane with thickness of ~2 µm demonstrating binary propylene permeance of $2.3x10^{-8}$ mol/m^2.s.Pa with separation factor of 50. Although the rapid thermal deposition method can prepare ZIF-8 membrane in a short period of time (~10 minutes), one of the disadvantages as compared to the counter diffusion method is that it is often difficult to identify and heal the defect of the membrane. On the other hand, the counter diffusion method enables the defect of the membranes to be identified and healed without disassembling the membrane modules.

J. Caro's group [61, 85, 91] has prepared ZIF-8 membranes utilizing different approaches, some as mentioned earlier in this manuscript. For example, *in-situ* preparation on titania support [61], secondary seeded growth using polyethyleneimine as the coupling agent [91], and synthesis of ZIF-8 on support modified poly-dopamine functionalized stainless steel nets [85]. Though these ZIF-8 membranes have been successfully prepared using conventional supports and showing promising separation selectivity, they have not resulted in high permeability when compared to modified support such as stainless steel nets. This is most probably due to the large flow resistance of gas transport through the conventional thick ceramic supports (~1 to 2 mm). As reported, both membranes synthesized on conventional supports exhibited H_2 permeance of ~10^{-8} mol/m^2.s.Pa while stainless steel net support demonstrated H_2 permeance of ~10^{-5} mol/m^2.s.Pa.

3.2. Moisture instability and easily induced cracks

Generally, metal-ligand coordination bonds of MOFs are not as strong as the Si-O covalent bonds in zeolite membranes, thereby, moisture instability and cracks are more likely to form. One of the reasons for cracks formation is attributed to the stress on the film due to mismatch between both thermal expansion coefficient of the support and the MOFs membrane. Guerrero et. al. [79] prevented crack in their HKUST-1 membrane by slowly cooling down the autoclaves from 120°C to 60°C at 1°C/min and then naturally to room temperature. The membranes need to be dried in order for the activation of its channels. They attempted drying (activation of pores) at room temperature or at elevated temperature, however, cracks were obviously seen. Since the magnitude of the capillary stress in the membranes is proportional to the rate of evaporation, they evaporated the water at 40°C under nearly saturated conditions thereby eliminated the cracks completely.

Several attempts have been performed by Dong et al. [92] to eliminate the micro-cracks of their ZIF-78 membrane. For instance, immersed the membrane in fresh methanol for 12 hours followed by drying at 60°C under vacuum, in spite of that, micro-cracks were still observed likely due to the rapid methanol drying process. They have also performed drying at 40°C under saturated methanol environment for 3 days which does not result in optimistic molecular sieve behaviour. The author speculated that with pure methanol used for solvent exchange for DMF removal, diffusion of DMF will be too fast due to high concentration gradient. Therefore, they prepared a series of methanol-DMF mixtures with 25, 50, 75 and 100% of methanol concentrations. As shown in **Figure 7**, they immerse the ZIF-78 membrane in these solutions in turn for solvent exchange followed by a slow evaporation of methanol drying process. The as prepared ZIF-78 membrane for further gas separation has achieved H_2/CO_2 ideal and binary selectivity of 11.0 and 9.5, respectively.

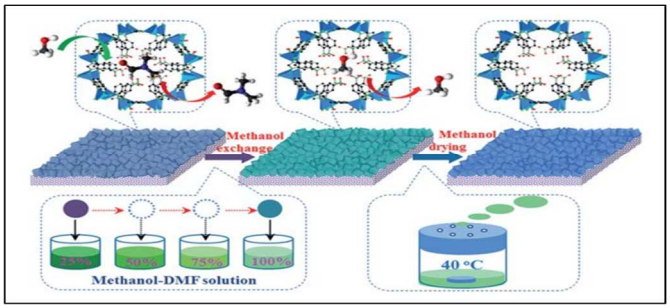

Fig 7. Schematic diagram of the activating process of the ZIF-78 membrane. [92]

Post synthetic modifications (PSM) can also be implemented to improve MOFs moisture stability. Nguyen and Cohen [93] have demonstrated that hydrophobic properties can be incorporated within a MOF. Amine containing MOFs can readily undergo PSM to form amide functionalized MOFs. Hypothesis was that the introduction of hydrophobic alkyl chains could improve moisture resistance and change the physical properties (i.e. hydrophobicity) of the MOFs. Through integration of medium to long hydrophobic alkyl groups within IRMOF-3, the moisture sensitive IRMOF-3 could be shielded from moisture by changing its property to hydrophobic. Within the same study, a more chemically robust MOF, MIL-53(Al)-NH_2, were examined to check how the same functional groups would affect its properties. It was found that MIL-53(Al) modified with longer alkyl substituents appear to possess super-hydrophobic properties with contact angles greater than 150°.

On the contrary, Yoo et al. [94] improved the crack resistance and moisture stability of IRMOF-3 *via* surfactant assisted drying and post synthetic modifying method. As illustrated in **Figure 8**, IRMOF-1 seeds were initially prepared on graphite coated alumina *via* microwave assisted seeding followed by formation of IRMOF-3 membranes. IRMOF-3-AM6 membranes were prepared by post-synthetically modifying the IRMOF-3 membranes with heptanoic anhydride (AM6). At first, they have studied two different non-ionic surfactants for elimination of cracks, they are P123 and Span 80. Cracks are substantially reduced when P123 was added to the final drying stage, while addition of Span 80 exhibited no macroscopic crack. It was hypothesized that smaller hydrophilic head groups of Span 80 can interact favourably with surface of IRMOF-3 as compared to bulkier hydrophilic groups of P123, resulting in better performance of Span 80 as compared to P123. IRMOF-3 has switched from hydrophilic to hydrophobic after dried in the presence of Span 80.

Hydrophobic MOFs with better moisture stability will repel water molecules subsequently preventing water molecules to displace its carboxylic groups. Following the study of surfactant assisted drying, IRMOF-3 was post synthetically modified with AM6 to change its pore size and property of the membrane. The effective pore size has decreased and the surface property of the post-synthetically modified IRMOF-3-AM6 was changed with ~91% of amine groups converted to amides based on TGA characterizations. After modification with hydrophobic anhydrides, the moisture stability of IRMOF-3 was drastically improved.

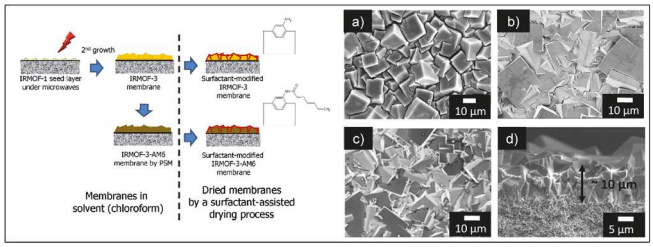

Fig 8. Schematic illustration of the fabrication of crack-free MOF membranes (IRMOF-3 and IRMOF-3-AM6 membranes) using a surfactant-assisted drying process (Left). SEM images of IRMOF-3 membranes after drying (a) without surfactant, (b) with a triblock copolymer, P-123, and (c) Span 80. The cross-sectional view (d) is from the membrane dried in the presence of Span 80 with thickness of ~10 µm (Right). [94]

Layer-by-layer (LBL) growth of MOFs thin films involves repeated cycles of immersion of a membrane substrate in solutions with both metal salts and organic linker. The substrate will be rinsed with solvent to remove the un-reacted components in between their deposition steps. Here, Lee et al. [95] synthesized Ni-MOF-74 membranes *via* a combined layer-by-layer seeding and secondary growth technique and describe their procedure in preventing crack formation of MOF membranes. They showed that an optimum concentration of solution (8.0 mmol $Ni(CH_3COO)_2$ and 4.0 mmol 2,5-Dihydroxyterephthalic acid) was needed in order to obtain a crack free Ni-MOF-74 membrane together with four alternating immersion cycles. They concluded that a more concentrated solution provides sufficient nutrition for the growth of crystals to help achieve crack free Ni-MOF-74 membranes, however, solution with excessively high concentration would also lead to degradation of membrane performance. The single gas permeation test on the Ni-MOF-74 has resulted in H_2/N_2, H_2/CO_2, and H_2/CH_4 ideal selectivity of 3.1, 9.1, and 2.9, respectively. With CO_2 permeance deviates from the linear relation, it can be ascribed to the surface diffusion due to strong adsorption affinity of CO_2 to Ni-MOF-74 membrane. The detailed explanation for its adsorption affinity could be found in detail in the literature [95].

4. Outlook and Perspective

Due to the recentness of MOFs materials, their real potential for membrane gas separation such as H_2 separation, natural gas purification (CO_2 separation over CH_4), and CO_2 reduction from flue gas have not been fully explored. In order to evaluate these potential MOFs membranes for CO_2 separation, numerous properties such as CO_2 adsorption affinity, pore size and framework structure, and thermal and humidity stability need to be thoroughly investigated. ZIFs, a subclass of MOFs, with their proven unusual stability coupled with various range of pore sizes seem to have great potential for CO_2 separation [96]. However, separation of gas molecules based on appropriate pore size is not as simple as it seem due to its framework structure flexibility which is against the molecular sieving mechanism [22, 61, 88]. For example, recent reported results of ZIF-7 [88] with pore aperture of 0.30 nm designated that even large molecules like CH_4 (0.38 nm) are able to permeate through the membrane, implying that it may be useful to pursue ZIFs with smaller aperture. On the other hand, Bux et al. [91] stated that a sharp cut off permeance have not been observed for ZIF membranes, due to the flexible nature of its framework. The author demonstrated only a sharp cut off permeance of H_2 and C_3H_8 with ZIF-8 pore aperture of 0.34 nm, indicating that the large derivations of the experiment separation factors as compared to those predicted from rigid framework structure models were not all attributed to mass transfer through grain boundaries or defects. This is in contrary to those of zeolite membranes that exhibit "molecular sieving properties", with substantial reduction in permeance for molecules with kinetic diameter greater than its pore size.

MOFs membranes are still capped within research at current stage, the large scales of their applications are not yet ready to be envisioned with present existing commercial technology. Nonetheless, there are researchers working on the scalability of MOFs membranes [97-99]. In particular, Brown et al. [97] reported a route which could mainly overcome the limitation of current synthesis process, a notable step towards accomplishing scalable MOF membranes. Their method involves combining two solvent interfacial approach for positional control over ZIF-8 membrane formation on the polymeric hollow fibres, a micro-fluidic approach, to replenish and recycle the reactants for membranes fabrication. Their continuous ZIF-8 membranes fabricated on poly(amine-imide) hollow fibres achieved highest H_2/C_3H_8 and C_3H_6/C_3H_8 separation factors of 370 and 12, respectively. Mao et al. [98] prepared continuous HKUST-1 membranes by filtering copper nitrate through the PVDF hollow fibres, followed by immersing the PVDF hollow fibre in a container filled with trimesic acid with regulating pump. A continuous HKUST-1 membrane with thickness of 3 µm was obtained typically after ~40 minutes. Their HKUST-1 membrane achieved H_2/CO_2, H_2/N_2, and H_2/CH_4 separation factor of 8.1, 6.5, and 5.4, respectively. On the other hand, Fan et al. [99] adopted the electro spinning technology for seeding purposes. A high voltage will be applied to the metallic tip to draw the viscous solution into the fibres where the macroporous SiO_2 support will serve as the collector. With the advantage of this electro spinning technology, this method could be applied to all different kinds of support with potential of large area processing as well. In spite of the fact that researchers are working on scalability of MOFs membranes, till now, no firm

conclusion on the scalability of MOFs membranes could be drawn. Therefore, more open ideas and promising results are needed in order to enable the research community to resolve this issue.

Despite the development of MOFs membranes made over several years, MOFs still have further potential for improvements. Nonetheless, it is constructive to compare different types of MOFs membranes in terms of their gas separation performances. **Table 1.** and **Table 2.** presents the single gas permeation and selectivities of several gases on different MOFs membranes, respectively, showing attractively high permeances though their permselectivity is still relatively moderate only.

Conclusions

MOFs, the young child of porous materials, are considered to be relatively new despite the research made over the past decade. Though several MOFs membranes have been synthesized by researchers [91, 100-106], the permeability and selectivity of these membranes were not found to be outstandingly attractive. This could be due to the nature of MOFs with moderate selectivity, membrane defects caused by handling issue and the unfavourable orientation of crystals in the membrane. There are still considerable potential for improvement in the preparation of MOFs membranes, main concerns are about overcoming its easily crack formation and improving its separation performance. Great care must be taken not only to the synthesis of MOFs membranes, but also the activation and characterization for having fair and unbiased membranes comparison. In the case of membrane separations, the development of MOFs membranes that are reproducible for scaling up is still a major issue in future research. Furthermore, the final curtain for MOFs membranes should not be a calculated selectivity using single component gas permeances, but it should be selectively capturing one component from the other contaminants in a harsh and real operating environments (etc. hot flue gas stream). Confidently, further research would lead to stronger optimisms that MOFs can overcome its intrinsic limitations.

Table 1. Summary of Single Gas Permeances of MOFs membranes

MOF	T (°C)	Pore aperture (nm)	Permeances (10^8 mol/m^2.s.Pa) at 1 bar											Ref.
			H_2	CO_2	N_2	O_2	CO	CH_4	SF_6	He	C_2H_6	C_3H_6	C_3H_8	
MOF-5	25	1.4	280	65	80	-	-	105	42	-	-	-	-	63
MOF-5	25	1.4	130	33	40	-	-	55	22	-	-	-	-	63
MOF-5	25	1.4	80	25	30	-	-	39	-	-	-	-	-	77
MOF-5	25	1.4	44	10	13	-	13	-	4.2	30	-	-	-	107
ZIF-8	25	0.34	-	2430	-	-	-	472	-	-	-	-	-	69
ZIF-8	25	0.34	-	1690	-	-	-	242	-	-	-	-	-	69
ZIF-8[a]	20	0.34	-	-	-	-	-	-	-	-	-	1.85	0.02	76
ZIF-8[a]	150	0.34	-	-	-	-	-	-	-	-	-	1.10	0.06	76
ZIF-8	25	0.34	17.5	4.5	2	5.5	-	2	-	-	-	-	-	78
ZIF-8	100	0.34	2660	302	173	-	-	108	-	-	-	-	6.01	85
ZIF-8[b]	25	0.34	99	1.7~9.8[a]	31	-	-	25	-	-	-	-	-	108
ZIF-8	25	0.34	35	15	9	-	-	8	-	-	7	1	0.07	109
ZIF-8	25	0.34	110	22	17.5	-	-	18	-	-	-	-	-	110
ZIF-8	25	0.34	17	-	3	-	-	-	-	-	-	-	-	111
ZIF-8	25	0.34	154	40	14	-	-	12	-	-	9	-	0.14	112
ZIF-8	25	0.34	-	-	-	-	-	-	-	-	-	2.0788	0.0546	113
ZIF-8	35	0.34	47.2	12.2	4.46	-	-	4.17	0.0291	19.1	-	-	-	114
ZIF-7	200	0.29	7.4	1.1	1.1	-	-	1.2	-	-		-	-	88
ZIF-7	220	0.29	4.55	0.35	0.22	-	-	0.31	-	-	-	-	-	115
ZIF-7[c]	25	0.29	45.7	4.77	-	-	-	-	-	-	-	-	-	116
ZIF-7[c]	150	0.29	30.5	1.67	-	-	-	-	-	-	-	-	-	116
ZIF-22	50	0.29	20	2.4	2.8	2.8	-	3	-	-	-	-	-	80
ZIF-69	25	0.44	6.5	2.5	-	-	1.1	1.7	0.5	-	-	-	-	117
ZIF-69	25	0.44	-	2.36	1.06	-	0.82	0.86	-	-	-	-	-	118
ZIF-90	200	0.35	25	3.5	2	-	-	1.7	-	-	-	-	-	84
ZIF-90	200	0.35	25	3	2	-	-	1.5	-	-	-	-	-	119
ZIF-90[d]	200	0.35	21	1.5	1.2	-	-	1.2	-	-	-	-	-	119
ZIF-90	225	0.35	31	3.75	-	-	-	2.0	-	-	1.0	-	~0.9	120

ZIF-90[e]	225	0.35	29.5	1.75	-	-	-	0.8	-	-	~0.3	-	~0.2	120
ZIF-95	325	0.37	246	7.04	22.7	-	-	16.1	-	-	-	-	3.69	106
HKUST-1	25	0.9	74.8	14.8	20	-	-	25.7	-	-	-	-	-	73
HKUST-1	25	0.9	200	50	50	-	-	80	-	-	-	-	-	79
HKUST-1	190	0.9	110	20	15	-	-	20	-	-	-	-	-	79
HKUST-1[f]	25	0.9	0.127	0.0281	0.0276	-	-	0.0163	-	-	-	-	-	86
HKUST-1	25	0.9	18	4	4	4	-	6	-	-	-	-	-	121
MMOF	25	0.32	1.8	0.4	0.4	-	-	-	-	1.4	-	-	-	87
MMOF	190	0.32	0.2	0.04	0.01	-	-	-	-	0.3	-	-	-	87
bio-MOF-1	25	NA	-	119	-	-	-	46	-	-	-	-	-	122
bio-MOF-13	22	0.32-0.64	-	310-406	-	-	-	82-131	-	-	-	-	-	123
bio-MOF-14	22	0.16-0.40	-	416-455	-	-	-	118-141	-	-	-	-	-	123

Table 2. Summary of Single Gas Selectivities of MOFs membranes

MOF	T (°C)	Pore aperture	Permeances (10^8 mol/m^2.s.Pa) at 1 bar											Ref.
			H_2/CO_2	H_2/N_2	H_2/O_2	H_2/CO	H_2/CH_4	H_2/SF_6	H_2/He	H_2/C_2H_6	H_2/C_3H_8	CO_2/CH_4	C_3H_6/C_3H_8	
MOF-5	25	1.4	4.3	3.5	-	-	2.7	6.7	-	-	-	0.6	-	63
MOF-5	25	1.4	3.9	3.3	-	-	2.4	5.9	-	-	-	0.6	-	63
MOF-5	25	1.4	3.2	2.7	-	-	2.1	-	-	-	-	0.6	-	77
MOF-5	25	1.4	4.4	3.4	-	3.4	-	10.5	1.5	-	-	-	-	107
ZIF-8	25	0.34	-	-	-	-	-	-	-	-	-	5.1	-	69
ZIF-8	25	0.34	-	-	-	-	-	-	-	-	-	7.0	-	69
ZIF-8[a]	20	0.34	-	-	-	-	-	-	-	-	-	-	92.5	76
ZIF-8[a]	150	0.34	-	-	-	-	-	-	-	-	-	-	18.3	76
ZIF-8	25	0.34	3.9	8.8	3.2	-	8.8	-	-	-	-	2.3	-	78
ZIF-8	100	0.34	8.8	15.4	-	-	24.6	-	-	-	442.6	2.8	-	85
ZIF-8[b]	25	0.34	10.1-58.2	3.2	-	-	4.0	-	-	-	-	-	-	108
ZIF-8	25	0.34	2.3	3.9	-	-	4.4	-	-	5.0	500.0	1.9	14.3	109
ZIF-8	25	0.34	5.0	6.3	-	-	6.1	-	-	-	-	1.2	-	110
ZIF-8	25	0.34	-	5.7	-	-	-	-	-	-	-	-	-	111
ZIF-8	25	0.34	3.9	11.0	-	-	12.8	-	-	17.1	1100.0	3.3	-	112
ZIF-8	25	0.34	-	-	-	-	-	-	-	-	-	-	38.1	113
ZIF-8	35	0.34	3.9	10.6	-	-	11.3	1622.0	2.5	-	-	2.9	-	114
ZIF-7	200	0.29	6.7	6.7	-	-	6.2	-	-	-	-	0.9	-	88
ZIF-7	220	0.29	13.0	20.7	-	-	14.7	-	-	-	-	1.1	-	115
ZIF-7[c]	25	0.29	9.6	-	-	-	-	-	-	-	-		-	116
ZIF-7[c]	150	0.29	18.3	-	-	-	-	-	-	-	-	-	-	116
ZIF-22	50	0.29	8.3	7.1	7.1	-	6.7	-	-	-	-	0.8	-	80
ZIF-69	25	0.44	2.6	-	-	5.9	3.8	13.0	-	-	-	1.5	-	117
ZIF-69	25	0.44	-	-	-	-	-	-	-	-	-	2.7	-	118
ZIF-90	200	0.35	7.1	12.5	-	-	14.7	-	-	-	-	2.1	-	84
ZIF-90	200	0.35	8.3	12.5	-	-	16.7	-	-	-	-	2.0	-	119
ZIF-90[d]	200	0.35	14.0	17.5	-	-	17.5	-	-	-	-	1.3	-	119
ZIF-90	225	0.35	8.3	-	-	-	15.5	-	-	31.0	34.4	1.9	-	120

ZIF-90[e]	225	0.35	16.9	-	-	-	36.9	-	-	98.3	147.5	2.2	-	120
ZIF-95	325	0.37	34.9	10.8	-	-	15.3	-	-	-	66.7	0.4	-	106
HKUST-1	25	0.9	5.1	3.7	-	-	2.9	-	-	-	-	0.6	-	73
HKUST-1	25	0.9	4.0	4.0	-	-	2.5	-	-	-	-	0.6	-	79
HKUST-1	190	0.9	5.5	7.3	-	-	5.5	-	-	-	-	1.0	-	79
HKUST-1[f]	25	0.9	4.5	4.6	-	-	7.8	-	-	-	-	1.7	-	86
HKUST-1	25	0.9	4.5	4.5	4.5	-	3.0	-	-	-	-	0.7	-	121
MMOF	25	0.32	4.5	4.5	-	-	-	-	1.3	-	-	-	-	87
MMOF	190	0.32	5.0	20.0	-	-	-	-	0.7	-	-	-	-	87
bio-MOF-1	25	NA	-	-	-	-	-	-	-	-	-	2.6	-	122
bio-MOF-13	22	0.32-0.64	-	-	-	-	-	-	-	-	-	3.1 - 3.8	-	123
bio-MOF-14	22	0.16-0.40	-	-	-	-	-	-	-	-	-	3.2 - 3.5	-	123

[a] Refers to ZIF-8 synthesized for 4 hours *via* counter diffusion based *in-situ* method. [b] Refers to CO_2 permeances dropped with time from 9.8 x 10^{-8} mol/m^2.s.Pa at 0.1 hour to 1.7 x 10^{-8} mol/m^2.s.Pa reaches equilibrium at 12 hours. [c] Refers to binary gas permeation measurement with 1:1 H_2/CO_2 mixture. [d] Refers to post functionalized ZIF-90 with ethanolamine. [e] Refers to post functionalized ZIF-90 with APTES ((3-Aminopropyl)triethoxysilane). [f] Refers to HKUST-1 thin film displaying permeances with unit of 10^0 mol/m^2.s.Pa at 1 bar.

RSC Advances RSCPublishing

REVIEW ARTICLE

Acknowledgment

We would like to thank the Ministry of Higher Education Malaysia through Long term Research Grant Scheme (LRGS) (A/C number 2110226-113-00) for the financial support given.

Notes and references

a. Low Carbon Economy Group, Chemical Engineering Discipline, School of Engineering, Monash University, 46150 Bandar Sunway, Selangor, Malaysia;

b. Department of Materials Engineering, Monash University, Clayton, Victoria 3800, Australia;

c. Low Carbon Economy Group, School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, Penang, Malaysia.

*Corresponding author. Tel: +603-55146234; Fax: +603-55146207; E-mail: chai.siang.piao@monash.edu

1. A. M. Fracaroli, H. Furukawa, M. Suzuki, M. Dodd, S. Okajima, F. Gándara, J. A. Reimer and O. M. Yaghi, *J. Am. Chem. Soc.*, 2014, **136**, 8863-8866.
2. F. Gándara, H. Furukawa, S. Lee and O. M. Yaghi, *J. Am. Chem. Soc.*, 2014, **136**, 5271-5274.
3. B. Li, H.-M. Wen, H. Wang, H. Wu, M. Tyagi, T. Yildirim, W. Zhou and B. Chen, *J. Am. Chem. Soc.*, 2014, **136**, 6207-6210.
4. Z. Zhang, Z.-Z. Yao, S. Xiang and B. Chen, *Energ. Environ. Sci.*, 2014, **7**, 2868-2899.
5. Z.-H. Xuan, D.-S. Zhang, Z. Chang, T.-L. Hu and X.-H. Bu, *Inorg. Chem.*, 2014, **53**, 8985-8990.
6. H. Oh, I. Savchenko, A. Mavrandonakis, T. Heine and M. Hirscher, *ACS Nano*, 2013, **8**, 761-770.
7. T. Rodenas, M. van Dalen, E. García-Pérez, P. Serra-Crespo, B. Zornoza, F. Kapteijn and J. Gascon, *Adv. Funct. Mater.*, 2014, **24**, 268-268.
8. A. Huang, Y. Chen, Q. Liu, N. Wang, J. Jiang and J. Caro, *J. Membrane. Sci.*, 2014, **454**, 126-132.
9. D. Wang, T. Zhao, Y. Cao, S. Yao, G. Li, Q. Huo and Y. Liu, *Chem. Commun.*, 2014, **50**, 8648-8650.
10. H. Alawisi, B. Li, Y. He, H. D. Arman, A. M. Asiri, H. Wang and B. Chen, *Cryst. Growth. Des.*, 2014, **14**, 2522-2526.
11. X. Duan, Q. Zhang, J. Cai, Y. Yang, Y. Cui, Y. He, C. Wu, R. Krishna, B. Chen and G. Qian, *J. Mater. Chem. A.*, 2014, **2**, 2628-2633.
12. M. J. Katz, J. E. Mondloch, R. K. Totten, J. K. Park, S. T. Nguyen, O. K. Farha and J. T. Hupp, *Angew. Chem. Int. Edit.*, 2014, **53**, 497-501.
13. A. M. Rasero-Almansa, A. Corma, M. Iglesias and F. Sánchez, *ChemCatChem*, 2014, **6**, 1794-1800.
14. K. Mo, Y. Yang and Y. Cui, *J. Am. Chem. Soc.*, 2014, **136**, 1746-1749.
15. J. L. Harding and M. M. Reynolds, *J. Mater. Chem. B.*, 2014, **2**, 2530-2536.
16. A. Dhakshinamoorthy and H. Garcia, *Chem. Soc. Rev.*, 2014, **43**, 5750-5765.
17. J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang and C.-Y. Su, *Chem. Soc. Rev.*, 2014, **43**, 6011-6061.
18. N. Stock and S. Biswas, *Chem. Rev.*, 2011, **112**, 933-969.
19. S. Kitagawa, R. Kitaura and S. i. Noro, *Angew. Chem. Int. Edit.*, 2004, **43**, 2334-2375.
20. G. Férey, *Chem. Soc. Rev.*, 2008, **37**, 191-214.
21. D. Zacher, O. Shekhah, C. Wöll and R. A. Fischer, *Chem. Soc. Rev.*, 2009, **38**, 1418-1429.
22. J.-R. Li, R. J. Kuppler and H.-C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477-1504.
23. J. R. Long and O. M. Yaghi, *Chem. Soc. Rev.*, 2009, **38**, 1213-1214.
24. M. Shah, M. C. McCarthy, S. Sachdeva, A. K. Lee and H.-K. Jeong, *Ind. Eng. Chem. Res.*, 2012, **51**, 2179-2199.
25. H.-C. J. Z. a. S. Kitagawa, *Chem. Soc. Rev.*, 2014, **43**, 5415-5418.
26. Z. Y. Yeo, T. L. Chew, P. W. Zhu, A. R. Mohamed and S.-P. Chai, *J. Nat. Gas Chem.*, 2012, **21**, 282-298.
27. D. F. Sanders, Z. P. Smith, R. Guo, L. M. Robeson, J. E. McGrath, D. R. Paul and B. D. Freeman, *Polymer*, 2013, **54**, 4729-4761.
28. Y. Zhang, J. Sunarso, S. Liu and R. Wang, *Int. J. Greenh. Gas. Con.*, 2013, **12**, 84-107.
29. P. Bernardo and E. Drioli, *Petrol. Chem.*, 2010, **50**, 271-282.
30. J. Caro, *Current Opinion in Chemical Engineering*, 2011, **1**, 77-83.
31. J. Caro and M. Noack, in *Advances in Nanoporous Materials*, ed. E. Stefan, Elsevier, 2010, vol. Volume 1, pp. 1-96.
32. T. Tomita, K. Nakayama and H. Sakai, *Micropor. Mesopor. Mat.*, 2004, **68**, 71-75.
33. Y. Cui, H. Kita and K. Okamoto, *Chem. Commun.*, 2003, 2154-2155.
34. S. Himeno, T. Tomita, K. Suzuki, K. Nakayama, K. Yajima and S. Yoshida, *Ind. Eng. Chem. Res.*, 2007, **46**, 6989-6997.
35. H. Vinh-Thang and S. Kaliaguine, *Chem. Rev.*, 2013, **113**, 4980-5028.

36. M. Rezakazemi, A. Ebadi Amooghin, M. M. Montazer-Rahmati, A. F. Ismail and T. Matsuura, *Prog. Polym. Sci.*, 2014, **39**, 817-861.
37. C. Duan, X. Jie, D. Liu, Y. Cao and Q. Yuan, *J. Membrane. Sci.*, 2014, **466**, 92-102.
38. E. V. Perez, K. J. Balkus Jr, J. P. Ferraris and I. H. Musselman, *J. Membrane. Sci.*, 2014, **463**, 82-93.
39. Y. Liu, S. Li, X. Zhang, H. Liu, J. Qiu, Y. Li and K. L. Yeung, *Inorg. Chem. Commun.*, 2014, **48**, 77-80.
40. J. Campbell, G. Szekely, R. P. Davies, D. C. Braddock and A. G. Livingston, *J. Mater. Chem. A.*, 2014, **2**, 9260-9271.
41. D. Wu, G. Maurin, Q. Yang, C. Serre, H. Jobic and C. Zhong, *J. Mater. Chem. A.*, 2014, **2**, 1657-1661.
42. S. Sorribas, B. Zornoza, C. Téllez and J. Coronas, *J. Membrane. Sci.*, 2014, **452**, 184-192.
43. J. O. Hsieh, K. J. Balkus Jr, J. P. Ferraris and I. H. Musselman, *Micropor. Mesopor. Mat.*, 2014, **196**, 165-174.
44. J. Jiang, *Current Opinion in Chemical Engineering*, 2012, **1**, 138-144.
45. J. Gascon and F. Kapteijn, *Angew. Chem. Int. Edit.*, 2010, **49**, 1530-1532.
46. C. Cui, Y. Liu, H. Xu, S. Li, W. Zhang, P. Cui and F. Huo, *Small*, 2014, **10**, 3672-3676.
47. G. Lu, C. Cui, W. Zhang, Y. Liu and F. Huo, *Chem. Asian. J.*, 2013, **8**, 69-72.
48. M. E. Silvestre, M. Franzreb, P. G. Weidler, O. Shekhah and C. Wöll, *Adv. Funct. Mater.*, 2013, **23**, 1210-1213.
49. M. C. So, S. Jin, H.-J. Son, G. P. Wiederrecht, O. K. Farha and J. T. Hupp, *J. Am. Chem. Soc.*, 2013, **135**, 15698-15701.
50. D. Witters, S. Vermeir, R. Puers, B. F. Sels, D. E. De Vos, J. Lammertyn and R. Ameloot, *Chem. Mater.*, 2013, **25**, 1021-1023.
51. J. T. Joyce, F. R. Laffir and C. Silien, *J. Phys. Chem. C.*, 2013, **117**, 12502-12509.
52. D. Y. Lee, E.-K. Kim, C. Y. Shin, D. V. Shinde, W. Lee, N. K. Shrestha, J. K. Lee and S.-H. Han, *RSC Adv.*, 2014, **4**, 12037-12042.
53. P. Horcajada, C. Serre, D. Grosso, C. Boissière, S. Perruchas, C. Sanchez and G. Férey, *Adv. Mater.*, 2009, **21**, 1931-1935.
54. M. Li and M. Dinca, *Chem. Sci.*, 2014, **5**, 107-111.
55. I. Hod, W. Bury, D. M. Karlin, P. Deria, C.-W. Kung, M. J. Katz, M. So, B. Klahr, D. Jin, Y.-W. Chung, T. W. Odom, O. K. Farha and J. T. Hupp, *Adv. Mater.*, 2014, n/a-n/a.
56. N. Campagnol, E. R. Souza, D. E. De Vos, K. Binnemans and J. Fransaer, *Chem. Commun.*, 2014.
57. N. Campagnol, T. Van Assche, T. Boudewijns, J. Denayer, K. Binnemans, D. De Vos and J. Fransaer, *J. Mater. Chem. A.*, 2013, **1**, 5827-5830.
58. O. Shekhah, J. Liu, R. A. Fischer and C. Woll, *Chem. Soc. Rev.*, 2011, **40**, 1081-1106.
59. D. Zacher, O. Shekhah, C. Woll and R. A. Fischer, *Chem. Soc. Rev.*, 2009, **38**, 1418-1429.
60. J. Yao and H. Wang, *Chem. Soc. Rev.*, 2014, **43**, 4470-4493.
61. H. Bux, F. Liang, Y. Li, J. Cravillon, M. Wiebcke and J. Caro, *J. Am. Chem. Soc.*, 2009, **131**, 16000-16001.
62. J. Yao, D. Dong, D. Li, L. He, G. Xu and H. Wang, *Chem. Commun.*, 2011, **47**, 2559-2561.
63. Y. Liu, Z. Ng, E. A. Khan, H.-K. Jeong, C.-b. Ching and Z. Lai, *Micropor. Mesopor. Mat.*, 2009, **118**, 296-301.
64. F. Cao, C. Zhang, Y. Xiao, H. Huang, W. Zhang, D. Liu, C. Zhong, Q. Yang, Z. Yang and X. Lu, *Ind. Eng. Chem. Res.*, 2012, **51**, 11274-11278.
65. T. Ben, C. Lu, C. Pei, S. Xu and S. Qiu, *Chem. Eur. J.*, 2012, **18**, 10250-10253.
66. N. Hara, M. Yoshimune, H. Negishi, K. Haraya, S. Hara and T. Yamaguchi, *RSC Adv.*, 2013, **3**, 14233-14236.
67. N. Hara, M. Yoshimune, H. Negishi, K. Haraya, S. Hara and T. Yamaguchi, *J. Membr. Sci.*, 2014, **450**, 215-223.
68. M. N. Shah, M. A. Gonzalez, M. C. McCarthy and H.-K. Jeong, *Langmuir*, 2013, **29**, 7896-7902.
69. S. R. Venna and M. A. Carreon, *J. Am. Chem. Soc.*, 2010, **132**, 76-78.
70. K. Li, D. H. Olson, J. Seidel, T. J. Emge, H. Gong, H. Zeng and J. Li, *J. Am. Chem. Soc.*, 2009, **131**, 10368-10369.
71. W. Zhou, H. Wu, T. J. Udovic, J. J. Rush and T. Yildirim, *J. Phys. Chem. A*, 2008, **112**, 12602-12606.
72. D. Fairen-Jimenez, S. A. Moggach, M. T. Wharmby, P. A. Wright, S. Parsons and T. Düren, *J. Am. Chem. Soc.*, 2011, **133**, 8900-8902.
73. J. Nan, X. Dong, W. Wang, W. Jin and N. Xu, *Langmuir*, 2011, **27**, 4309-4312.
74. Y. Hu, X. Dong, J. Nan, W. Jin, X. Ren, N. Xu and Y. M. Lee, *Chem. Commun.*, 2011, **47**, 737-739.
75. J. Nan, X. Dong, W. Wang and W. Jin, *Micropor. Mesopor. Mat.*, 2012, **155**, 90-98.
76. H. T. Kwon and H.-K. Jeong, *J. Am. Chem. Soc.*, 2013, **135**, 10763-10768.
77. Y. Yoo, Z. Lai and H.-K. Jeong, *Micropor. Mesopor. Mat.*, 2009, **123**, 100-106.
78. M. C. McCarthy, V. Varela-Guerrero, G. V. Barnett and H.-K. Jeong, *Langmuir*, 2010, **26**, 14636-14641.
79. V. V. Guerrero, Y. Yoo, M. C. McCarthy and H.-K. Jeong, *J. Mater. Chem.*, 2010, **20**, 3938-3943.
80. A. Huang, H. Bux, F. Steinbach and J. Caro, *Angew. Chem.*, 2010, **122**, 5078-5081.
81. Z. Xie, J. Yang, J. Wang, J. Bai, H. Yin, B. Yuan, J. Lu, Y. Zhang, L. Zhou and C. Duan, *Chem. Commun.*, 2012, **48**, 5977-5979.
82. S. Hermes, F. Schröder, R. Chelmowski, C. Wöll and R. A. Fischer, *J Am. Chem. Soc.*, 2005, **127**, 13744-13745.
83. E. Biemmi, C. Scherb and T. Bein, *J Am. Chem. Soc.*, 2007, **129**, 8054-8055.
84. A. Huang, W. Dou and J. Caro, *J. Am. Chem. Soc.*, 2010, **132**, 15562-15564.

85. A. Huang, Q. Liu, N. Wang and J. Caro, *J. Mater. Chem. A.*, 2014.
86. H. Guo, G. Zhu, I. J. Hewitt and S. Qiu, *J. Am. Chem. Soc.*, 2009, **131**, 1646-1647.
87. R. Ranjan and M. Tsapatsis, *Chem. Mater.*, 2009, **21**, 4920-4924.
88. Y. S. Li, F. Y. Liang, H. Bux, A. Feldhoff, W. S. Yang and J. Caro, *Angew. Chem.*, 2010, **122**, 558-561.
89. S. Zhou, X. Zou, F. Sun, F. Zhang, S. Fan, H. Zhao, T. Schiestel and G. Zhu, *J. Mater. Chem.*, 2012, **22**, 10322-10328.
90. Y. Yoo and H.-K. Jeong, *Chem. Commun.*, 2008, 2441-2443.
91. H. Bux, A. Feldhoff, J. Cravillon, M. Wiebcke, Y.-S. Li and J. Caro, *Chem. Mater.*, 2011, **23**, 2262-2269.
92. X. Dong, K. Huang, S. Liu, R. Ren, W. Jin and Y. S. Lin, *J. Mater. Chem.*, 2012, **22**, 19222-19227.
93. J. G. Nguyen and S. M. Cohen, *J Am. Chem. Soc.*, 2010, **132**, 4560-4561.
94. Y. Yoo, V. Varela-Guerrero and H.-K. Jeong, *Langmuir*, 2011, **27**, 2652-2657.
95. D.-J. Lee, Q. Li, H. Kim and K. Lee, *Micropor. Mesopor. Mat.*, 2012, **163**, 169-177.
96. K. S. Park, Z. Ni, A. P. Côté, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe and O. M. Yaghi, *P. Natl. Acad. Sci. USA*, 2006, **103**, 10186-10191.
97. A. J. Brown, N. A. Brunelli, K. Eum, F. Rashidi, J. R. Johnson, W. J. Koros, C. W. Jones and S. Nair, *Science*, 2014, **345**, 72-75.
98. Y. Mao, J. Li, W. Cao, Y. Ying, L. Sun and X. Peng, *ACS Appl. Mater. Interfaces.*, 2014, **6**, 4473-4479.
99. L. Fan, M. Xue, Z. Kang, H. Li and S. Qiu, *J. Mater. Chem.*, 2012, **22**, 25272-25276.
100. T.-H. Bae, J. S. Lee, W. Qiu, W. J. Koros, C. W. Jones and S. Nair, *Angew.Chem. Int. Edit.*, 2010, **49**, 9863-9866.
101. Y. Li, F. Liang, H. Bux, W. Yang and J. Caro, *J. Membr. Sci.*, 2010, **354**, 48-54.
102. A. Huang, W. Dou and J. r. Caro, *J. Am. Chem. Soc.*, 2010, **132**, 15562-15564.
103. Y. Pan, B. Wang and Z. Lai, *J. Membr. Sci.*, 2012.
104. H. Bux, C. Chmelik, R. Krishna and J. Caro, *J. Membr. Sci.*, 2011, **369**, 284-289.
105. A. Huang, N. Wang, C. Kong and J. Caro, *Angew. Chem. Int. Edit.*, 2012, **51**, 10551-10555.
106. A. Huang, Y. Chen, N. Wang, Z. Hu, J. Jiang and J. Caro, *Chem. Commun.*, 2012, **48**, 10981-10983.
107. Z. Zhao, X. Ma, Z. Li and Y. S. Lin, *J. Membr. Sci.*, 2011, **382**, 82-90.
108. G. Xu, J. Yao, K. Wang, L. He, P. A. Webley, C.-s. Chen and H. Wang, *J. Membr. Sci.*, 2011, **385–386**, 187-193.
109. Y. Pan and Z. Lai, *Chem. Commun.*, 2011, **47**, 10275-10277.
110. K. Tao, C. Kong and L. Chen, *Chem. Eng. J.*, 2013, **220**, 1-5.
111. L. Li, J. Yao, R. Chen, L. He, K. Wang and H. Wang, *Micropor. Mesopor. Mat.*, 2013, **168**, 15-18.
112. Y. Pan, B. Wang and Z. Lai, *J. Membr. Sci.*, 2012, **421–422**, 292-298.
113. H. T. Kwon and H.-K. Jeong, *Chem. Commun.*, 2013, **49**, 3854-3856.
114. D. Liu, X. Ma, H. Xi and Y. S. Lin, *J. Membr. Sci.*, 2014, **451**, 85-93.
115. Y. Li, F. Liang, H. Bux, W. Yang and J. Caro, *J. Membr. Sci.*, 2010, **354**, 48-54.
116. V. M. Aceituno Melgar, H. T. Kwon and J. Kim, *J. Membr. Sci.*, 2014, **459**, 190-196.
117. Y. Liu, E. Hu, E. A. Khan and Z. Lai, *J. Membr. Sci.*, 2010, **353**, 36-40.
118. Y. Liu, G. Zeng, Y. Pan and Z. Lai, *J. Membr. Sci.*, 2011, **379**, 46-51.
119. A. Huang and J. Caro, *Angew. Chem. Int. Edit.*, 2011, **50**, 4979-4982.
120. A. Huang, N. Wang, C. Kong and J. Caro, *Angew. Chem. Int. Edit.*, 2012, **51**, 10551-10555.
121. Y. Mao, W. Cao, J. Li, L. Sun and X. Peng, *Chem. Eur. J.*, 2013, **19**, 11883-11886.
122. J. A. Bohrman and M. A. Carreon, *Chem. Commun.*, 2012, **48**, 5130-5132.
123. Z. Xie, T. Li, N. L. Rosi and M. A. Carreon, *J. Mater. Chem. A.*, 2014, **2**, 1239-1241.

