Fuels of the Future

Guest Editors: Ben W.-L. Jang, Roger Gläser, Chang-jun Liu and Mingdong Dong

Editorial

Fuels of the Future
Ben W.-L. Jang, Roger Gläser, Chang-jun Liu and Mingdong Dong, Energy Environ. Sci., 2010
DOI: 10.1039/c003390c

Review

Ceramic membranes for gas processing in coal gasification
DOI: 10.1039/b924327e

Perspective

Solar hydrogen: fuel of the near future
Mario Pagliaro, Athanasios G. Konstandopoulos, Rosaria Ciriminna and Giovanni Palmisano, Energy Environ. Sci., 2010
DOI: 10.1039/b923793n

Communication

Room-temperature high-sensitivity detection of ammonia gas using the capacitance of carbon/silicon heterojunctions
Qingzhong Xue, Huijuan Chen, Qun Li, Keyou Yan, Flemming Besenbacher and Mingdong Dong, Energy Environ. Sci., 2010
DOI: 10.1039/b925172n

Papers

Selective catalytic oxidation of H_2S to elemental sulfur over V_2O_5/Zr-pillared montmorillonite clay
Kanattukara Vijayan Bineesh, Dong-Kyu Kim, Dong-Woo Kim, Han-Jun Cho and Dae-Won Park, Energy Environ. Sci., 2010
DOI: 10.1039/b921937d

Catalytic hydrothermal deoxygenation of palmitic acid
Jie Fu, Xiuang Lu and Phillip E. Savage, Energy Environ. Sci., 2010
DOI: 10.1039/b923198f

Biodiesel from meadowfoam (Limnanthes alba L.) seed oil: oxidative stability and unusual fatty acid composition
Bryan R. Moser, Gerhard Knothe and Steven C. Cermak, Energy Environ. Sci., 2010
DOI: 10.1039/b923740m

Removal of refractory organosulfur compounds via oxidation with hydrogen peroxide on amorphous Ti/SiO_x catalysts
M. Carmen Capel-Sanchez, Jose M. Campos-Martin and Jose L. G. Fierro, Energy Environ. Sci., 2010
DOI: 10.1039/b923795j

Cyanobacteria immobilised in porous silica gels: exploring biocompatible synthesis routes for the development of photobioreactors
Alexandre Léonard, Joanna C. Rooke, Christophe F. Meunier, Hugo Sarmento, Jean-Pierre Descy and Bao-Lian Su, Energy Environ. Sci., 2010
DOI: 10.1039/b923859j

Steam reforming of ethanol to H_2 over Rh/Y_2O_3: crucial roles of Y_2O_3 oxidizing ability, space velocity, and H_2/C
Xusheng Wu and Sibudjing Kawi, Energy Environ. Sci., 2010
DOI: 10.1039/b923978m

Selecting metal organic frameworks as enabling materials in mixed matrix membranes for high efficiency natural gas purification
Seda Keskin and David S. Sholl, Energy Environ. Sci., 2010
DOI: 10.1039/b923980b

Synthesis of renewable jet and diesel fuels from 2-ethyl-1-hexene
Benjamin G. Harvey and Roxanne L. Quintana, Energy Environ. Sci., 2010
DOI: 10.1039/b924004g

Depolymerization of lignocellulosic biomass to fuel precursors: maximizing carbon efficiency by combining hydrolysis with pyrolysis
DOI: 10.1039/b924621p

Synthesis of solar fuels by a novel photoelectrocatalytic approach
Claudio Ampelli, Gabriele Centi, Rosalba Passalaqua and Siglinda Perathoner, Energy Environ. Sci., 2010
DOI: 10.1039/b925470f

Effect of pore structure on Ni catalyst for CO_2 reforming of CH_4
Nannan Sun, Xia Wen, Feng Wang, Wei Wei and Yuhan Sun, Energy Environ. Sci., 2010
DOI: 10.1039/b925503f
The addition of nonpolymeric particles to polymer films represents an important avenue for enhancing the performance of polymeric membranes for gas separations. We examine the challenge of selecting metal organic frameworks (MOFs) for use in high performance mixed matrix membranes using a combination of atomistic and continuum modeling. We validate our models by comparing with experimental data for IRMOF-1/Matrimid membranes. We then identify a highly selective MOF that is predicted to greatly enhance the performance of Matrimid and a range of other polymers for CO2/CH4 separations. The methods we introduce will create many opportunities for selecting MOF/polymer combinations for mixed matrix membranes with useful properties for large volume separations.

1. Introduction

Energy-efficient separation of gas mixtures is of enormous industrial importance in fuel processing. The traditional methods of gas separation and purification include distillation, extraction, adsorption, stripping, solvent extraction, crystallization, cryogenics and membranes.1 Higher energy costs in recent decades have made the membrane-based gas separation processes even more economically competitive with traditional separation techniques. Application of membrane-based separations includes several industrial processes related to alternative fuels:2–7 carbon dioxide purification by removal of carbon dioxide; purification of hydrogen from syngas derived from coal or biomass gasification; purification of ethanol and other alcohols from fermentation broths; and air separation to enable oxyfuel firing of coal/gas. Among these processes the first one has a special importance since large resources of natural gas reservoirs are known with high levels of CO2 and other contaminants.8 Carbon dioxide not only reduces the energy content of natural gas but also becomes corrosive in the presence of water, creating problems for pipeline transport. It would be highly desirable to capture the CO2 released by purification of these natural gas resources in a form that is suitable for immediate geological reinjection rather than emitting this CO2 to the atmosphere. Therefore, development of robust materials as alternatives to polymer membranes to achieve CO2/CH4 separations with high gas selectivity and permeability would have important social and economic impacts on mitigation of carbon dioxide emissions.

The current membrane market for commercial gas separations is dominated by polymer membranes due to their ease of fabrication and low cost. Polymer membranes can be formed as flat sheets or as fine capillaries (hollow fibers) 50–500 µm in diameter. The production costs of a hollow fiber module are in the range of $2–5 per m², compared to $10–100 per m² for equivalent spiral wound modules. For this reason, most of today’s gas separation membranes are hollow fiber modules.7

Membranes with both high selectivity and high gas permeability are required to lower the cost of large scale membrane-based gas separation processes. A high selectivity is of limited value if the gas permeability is low since a membrane with these properties will require a large surface area. Unfortunately, polymer membranes

Broader context

Polymer membranes are a proven technology for large-volume gas separations that have enormous potential in a variety of energy-related applications. Unfortunately, a fundamental tradeoff between throughput and selectivity limits the performance that can be achieved with these membranes. A powerful strategy for overcoming this tradeoff is to create composite materials where filler particles are included in a polymer matrix. If the properties of the filler particles can be controlled, large increases in membrane performance are possible. Metal organic framework (MOF) materials offer a tantalizing prospect as filler particles, since many MOFs are known and the properties of the nanometre-scale pores in MOFs can be tuned with relative ease. The diversity of known MOFs and polymers, however, makes selection of promising MOF/polymer pairs challenging. We show for the first time that materials modeling can be used to tackle this problem by focusing on separations of carbon dioxide and methane, a process of importance in natural gas processing. Use of a MOF that was specifically selected to have strong diffusion-based selectivity for carbon dioxide over methane is predicted to create composite membranes with extraordinary performance. The methods demonstrated here will also be of use for materials selection for other large-volume gas separations.
possess a trade-off between selectivity and gas permeability. Robeson used large collections of experimental data to demonstrate the inverse relationship between selectivity and throughput of polymeric membranes. Freeman presented a theory showing that the upper bound on membrane performance described by Robeson is a natural consequence of the strong size sieving nature of the stiff chain glassy polymer materials whose properties generally define the upper bound. Developing membranes that can exceed Robeson’s upper bounds for permeability and selectivity has been the central focus of research in high performance membranes for the past two decades.

One way to overcome the selectivity/permeability trade-off of polymeric membranes is to fabricate membranes entirely from non-polymeric materials such as zeolites. Two zeolites, DDR and SAPO-34, have attracted significant attention for separation of CO2/CH4 mixtures, because these zeolites create films that are highly selective for CO2. Carbon molecular sieves and carbon nanotubes are other alternatives to polymeric materials. Unfortunately, scale up and high manufacturing costs present fundamental challenges in the commercial implementation of these membranes. Unlike membranes based on purely inorganic films, membranes that combine polymers and non-polymeric particles as composites show much greater promise for short-term commercial implementation. These so-called mixed matrix membranes (MMMs) are heterogeneous membranes in which organic/inorganic fillers are embedded into a polymer matrix. The most significant advantage of MMMS is that fabricating these membranes on large scales can readily be envisioned with relatively minor adaptation of existing commercial technology. Numerous MMMs have been reported by incorporating materials such as non-porous silica particles, carbon molecular sieves, zeolites, fullerences and carbon nanotubes into polymers.

In this paper, we consider the use of a relatively new family of nanoporous materials, metal organic frameworks (MOFs), as the dispersed component in MMMS. Metal organic frameworks are crystalline materials combining metal complexes with organic linkers to produce highly porous materials. MOFs have interesting properties such as very large surface areas, high porosities, and the lowest densities among known crystalline materials, which have created interest in using MOFs for gas storage and separation applications. An important advantage of MOFs over zeolites is the relative ease with which it is possible to generate multiple materials with varying pore sizes and functionalities by changing the combination of metal and organic linker during synthesis.

Incorporation of MOFs into polymers to make MMMS has not been extensively studied. The first MOF-based MMM containing copper(ii) biphienyl dicarboxylate triethylenediamine in poly (3-acetoxethylthiophene) synthesized by Yehia and coworkers showed an enhanced CH4 selectivity relative to the pure polymer. Zhang et al. incorporated Cu-4,4-bipyridine-hexafluorosilicate (Cu-BPY-HFS) into a Matrimid membrane to study the pure gas permeation of H2, N2, O2, CH4, and CO2 as well as the separation of CO2/CH4, H2/CO2 and CH4/N2 gas mixtures. Including the MOF in the polymer increased the ideal and mixture selectivity towards CH4 due to the affinity of Cu-BPY-HFS towards CH4. Recently, Perez et al. combined the widely studied MOF IRMOF-1 with Matrimid to study the same gas pairs mentioned above. Although the MOF did not lead to an increase in the membrane selectivity, the permeability of the MMM was up to 120% larger than the pure polymer. These initial experimental studies suggest that it is relatively easy to make defect free MMMS including MOFs, a situation that is in contrast to composites using zeolites and carbon molecular sieves as filler particles. This result is reasonable if there is good interfacial contact between MOF nanocrystals and polymer matrices, and the partially organic structure of MOFs makes this desirable outcome reasonable to expect.

A fundamental challenge in using MOFs in MMMS is to choose the appropriate polymer/MOF combinations for specific separations of interest. Even if only one polymer is considered, there are thousands of MOFs that could potentially be used as filler particles. As a result, models that can predict polymer/MOF combinations that will have particularly attractive performances are likely to play a critical role in focusing experimental efforts. Unfortunately, no previous attempts have been made to model these composite materials. This is largely because the information that is currently available regarding the diffusion of molecules through MOFs is very limited, and information of this kind is a prerequisite for predicting the properties of MMMS. In the past several years, we have used atomically-detailed models of MOFs to predict the performance of pure MOFs as membranes for a variety of gas separations. In this paper, we show that this information can also be used to effectively model MOF-based MMMS. We first validate our methods by comparing predictions of our models with experimental data from Matrimid/IRMOF-1 composites for pure gas permeation of H2, N2, CH4, and CO2. We then focus on a gas separation of tremendous economic and environmental significance, separation of CO2/CH4 mixtures, using Matrimid as the polymer matrix. We predict the performance of MOF/Matrimid composite membranes for six different MOFs. Our results show that this kind of modeling can identify MOFs that are predicted to have extraordinary properties for CO2/CH4 separations.

2. Methods

2.1 Mixing models for mixed matrix membranes

Accurately describing the transport of gas species through a mixed matrix medium is a mathematically complex problem. Designing a MMM-based gas separation process requires knowledge of the permeability of gas species through the continuous phase (the polymer matrix) and the dispersed phase (the filler particles). There are several models in the literature to predict the permeation of gas species through MMMS. Most of these existing models are adaptations of thermal and/or electrical conductivity models. In this paper, we use the Maxwell and Bruggeman permeation models to predict the permeabilities of gases through MMMS consisting of Matrimid and MOFs as polymer and as additives, respectively. Matrimid is a natural choice for initial modeling of mixed matrix membranes because it is a commercially available polymer that forms membranes with useful performance and it has been studied in mixed matrix membrane experiments. The Maxwell model describes the effective permeability (Peff) of a gas species in a MMM for a suspension of filler particles in a polymer matrix as
In this expression, $P_c$ and $P_d$ represent the gas permeabilities in the continuous and dispersed phases, respectively, and $\phi_d$ is the volume fraction of the dispersed phase. The Maxwell model is intended to be applicable for low filler loadings since it assumes that the streamlines associated with diffusive mass transport around filler particles are not affected by the presence of nearby particles. The Bruggeman model, which can be considered to be an improved version of the Maxwell model, accounts for these effects and defines the effective permeability ($P_{\text{eff}}$) as

$$P_{\text{eff}} = P_c \left[ \frac{P_d + 2P_c - 2\phi_d(P_c - P_d)}{P_d + 2P_c + \phi_d(P_c - P_d)} \right]. \quad (1)$$

Bouma et al. showed that Maxwell and Bruggeman models give similar results up to $\phi_d = 0.2$. Both of the models outlined above describe the permeation of a pure gas through a membrane. Once the effective permeabilities of two gas species are calculated, the ideal selectivity, $\alpha_{\text{ideal}}(i/j)$, is the ratio of pure gas permeabilities of each species:

$$\alpha_{\text{ideal}}(i/j) = \left( \frac{P_{\text{eff}}}{P_c} \right) \left( \frac{P_{\text{eff}}}{P_d} \right)^{-1/3} = (1 - \phi_d). \quad (2)$$

It is important to note that the Maxwell and Bruggeman models are functions of the volume fraction of filler particles but not the particle morphology or particle size. This implies that these models are applicable to situations where the filler particles are relatively isotropic and can be well dispersed in the polymeric matrix. Strong deviation from this situation would require modifications of these mixing models. These models also assume that the polymer/filler interfaces do not introduce voids into the composite material or substantially change the properties of the polymer. In all of the models considered below, we used Matrimid as the polymer and used experimental data to define the polymer permeability. This approach is reasonable for Matrimid and other potential polymers of interest because gas permeability data on a huge range of polymeric membranes has been measured experimentally. Similar experimental data is not available for MOFs, and a key ingredient of our results is that the gas permeabilities through MOFs were predicted from detailed atomistic simulations as explained in the following section.

Modeling mixture permeation through MMMs is more complicated than describing pure gas permeation since the gas permeabilities of each species can be affected by competition effects between the two species. Vu et al. described an approach that is based solely on parameters supplied by pure gas measurements and is only a function of the partial pressures of gas species. We use the dual mode/partial immobilization model to predict the permeabilities of CO$_2$ and CH$_4$ in their binary mixture through Matrimid:

$$P_i/L = \frac{k_i D_i}{L} \left( 1 + \frac{F_i K_i}{1 + \sum_{j=1} b_i p_j} \right). \quad (4)$$

In the case of negligible permeate pressure, $P_i$ is the permeability of species $i$ in the permeating mixture, $p_i$ is the partial pressure of the species $i$ at the feed side of the membrane, $L$ is the membrane thickness and the remaining variables are the parameters of the gas species in Matrimid which were taken from the work of Madden.

We only considered mixture permeation for CO$_2$/CH$_4$ mixtures in Matrimid/IRMOF-1 mixed matrix membranes. To do so, the permeabilities of CO$_2$/CH$_4$ mixtures through IRMOF-1 membranes were calculated using molecular simulations and mixing theories. These calculations were performed by predicting adsorption isotherms and transport diffusivities of CO$_2$/CH$_4$ mixtures using ideal adsorbed solution theory and Skoulidas-Sholl-Krishna methods, respectively. These calculations use atomistic calculations to define the adsorption isotherms and diffusivities of the single component gases, then use mixing theories to describe the properties of adsorbed mixtures from the known single component properties. Steady state permeance of CO$_2$/CH$_4$ mixtures through defect-free IRMOF-1 membranes was calculated by specifying the pressure and composition of the bulk gas mixture on the feed side and the pressure on the permeate side of membrane and finding the flux of each species iteratively. The details of these calculations have been described previously. Once the permeabilities of CO$_2$/CH$_4$ mixtures in Matrimid and IRMOF-1 are calculated separately, the Maxwell and Bruggeman models were used to predict the mixture permeabilities for mixed matrix membranes.

### 2.2 Predicting gas permeabilities through MOFs using atomically-detailed calculations

As mentioned above, little information is available regarding the diffusion of molecules in MOFs. In this work, we used results from atomically detailed simulations to provide this information for a variety of different MOFs. We examined IRMOF-1 (also known as MOF-5), which has a three dimensional cubic structure with pore sizes >10 Å in diameter, in order to compare with experimental data from MMMs using this MOF. IRMOF-1 is a member of a family of MOFs with similar pore structures but differing pore sizes. We also examined IRMOF-8, IRMOF-10, IRMOF-14, which have larger pore sizes than IRMOF-1. As an example of a MOF with slightly smaller pores we studied CuBTC (also known as HKUST-1) which has main channels ~9 Å in diameter surrounded by tetrahedral pockets with diameters of 5 Å. Finally, we examined the narrow pore MOF, Cu(hfi-pbb)(H$_2$hfi-pbb)$_5$, representing an interpenetrated structure with cages that are moderate in size relative to small gas molecules (~5.1 x 5.1 Å) connected by small windows (~3.5 x 3.2 Å) based on atom to atom distances in the reported crystal structure. We have recently reported a combination of molecular simulations and quantum chemistry calculations that predict that Cu(hfi-pbb)(H$_2$hfi-pbb)$_5$ has very high selectivity for CO$_2$ over CH$_4$ if used as a membrane because CO$_2$ diffuses much more rapidly than CH$_4$ in this MOF.

Our previous molecular simulation studies reported the single component adsorption isotherms of CO$_2$, CH$_4$ and H$_2$ in IRMOF-1 as a function of gas fugacity at 25 °C. Equilibrium molecular dynamics simulations were used to compute the loading dependent corrected diffusivities of the same three species when adsorbed as pure gases. The transport diffusivity ($D_j$) is then defined without any approximation in terms of the following:
corrected diffusivity ($D_t$) and the thermodynamic correction factor,$^{70}$ where the latter is a partial derivative relating the adsorbate concentration, $c$, and bulk phase fugacity, $f$. The thermodynamic correction factor is fully defined once the single component adsorption isotherm is known. The relationship between the transport and corrected diffusivity is

$$D_t(c) = D_o(c) \cdot \left( \frac{\partial \ln f}{\partial \ln c} \right)_T.$$  \hspace{1cm} (5)

Steady state fluxes ($J$) of species across a MOF crystal are calculated based on Fick’s law,$^{70}$

$$J = -D_t(c) \cdot \nabla c,$$  \hspace{1cm} (6)

where $\nabla c$ is the concentration gradient of the adsorbed species based on the difference between the feed and permeate side pressures of the membrane. In membrane applications, the flux is usually reported in the form of permeability, $P$, which relates the net flux to the pressure drop, $\Delta p$, and membrane thickness, $L$, by

$$P = \frac{J}{\Delta p / L}.$$  \hspace{1cm} (7)

Similar calculations were performed to calculate the pure gas permeabilities of CO$_2$, CH$_4$ and H$_2$ in IRMOF-8, -10, -14 and CuBTC and CO$_2$ and H$_2$ in Cu(hfipbb)(H$_2$hfipbb)$_{0.5}$. To calculate the permeability of CH$_4$ in Cu(hfipbb)(H$_2$hfipbb)$_{0.5}$, we used transition state theory (TST) as explained in Section 3.2.

3. Results

3.1 Comparison between models and experimental data for Matrimid/IRMOF-1 membranes

To examine the validity of our models, we first studied Matrimid/IRMOF-1 composite membranes, for which experimental data is available by Perez et al.$^{45}$ Perez et al. reported the amount of IRMOF fillers in polymer matrices in weight fraction. Therefore, when we make comparisons between our modelling results and experimental data of Perez et al., we use weight fraction for ease of comparison. In all other places, we prefer reporting the filler amounts in volume fractions since these are more widely used in describing mixed matrix membranes.

Initially, we compare the predictions of the Maxwell and Bruggeman models with experimental observations for pure gas permeation of H$_2$, CH$_4$, N$_2$ and CO$_2$. Permeation of these species through pure Matrimid and Matrimid/IRMOF-1 membranes were measured by Perez et al.$^{45}$ for a feed pressure of 2 atm at 35 °C. All of the molecular simulations described above for IRMOF-1 crystals were at 25 °C.$^{53}$ The adsorption and diffusion properties of these gases in IRMOF-1 change only slightly between 25 and 35 °C, so the temperature difference between these data sets is unlikely to be important as long as the MMM results are interpreted at the temperature of the polymer data. Molecular simulations of adsorption and diffusion of CO$_2$ performed at 25 and 35 °C in Cu(hfipbb)(H$_2$hfipbb)$_{0.5}$ (data not shown) showed that this temperature difference does not have a significant effect on the MMM results.

Pure gas permeabilities through Matrimid/IRMOF-1 membranes were predicted using eqns (1) and (2) and the results are compared with the experimental data in Fig. 1. There is a good agreement between the predictions of the models and experimental data. Both models slightly overestimate the gas permeability data compared to the experiment measurements. The Bruggeman model predicts higher gas permeabilities for the mixed matrix membranes than the Maxwell model, especially at higher IRMOF-1 loadings. This is a general property of these
two models. We used the Maxwell and Bruggeman models for membranes with IRMOF weight fractions of up to 30%. These models are expected to be more precise when the loading of the filler particles is small. The good agreement between the model predictions and the experimental data in Fig. 1 and 2, however, indicates that this model is appropriate for loadings at least as high as the IRMOF-based membranes reported by Perez et al.

The ideal selectivities of gas pairs within the Matrimid/IRMOF-1 membranes were calculated using the Maxwell model and eqn (3) and compared with the available experimental data in Fig. 2. Once again, the agreement between theory and experiments is good. For example, the ideal selectivity of H2 (CO2) from CH4 was measured as 112 (40.5) by experiments and predicted to be 110.9 (40.9) for a Matrimid membrane with 20% (w/w) IRMOF-1 loading. Separation of CH4 from N2 with Matrimid/IRMOF-1 membranes is unexceptional, resulting in ideal selectivities of ~0.9. The highest ideal selectivities are observed for separation of H2 from N2 and from CH4 for which both experiments and calculations give selectivities >100 for a Matrimid membrane with 10% (w/w) IRMOF-1 loading. Qualitatively, the Maxwell model concurs with the experimental observation that adding IRMOF-1 particles in Matrimid does not improve the selectivity of the pure Matrimid membrane. This outcome is a direct result of the low selectivity of the pure IRMOF-1 crystals as membranes, a result that was predicted by our earlier calculations.

It is also possible to compare our predictions for IRMOF-1 to experimental data from membranes made from dense IRMOF-1 films. Liu et al. recently prepared continuous, well intergrown IRMOF-1 films of porous α-alumina substrates. Our theoretical predictions agree well with the experimental results of CH4, H2, and N2 permeance through IRMOF-1 films and slightly overestimate the measured permeance values for CO2, indicating that our theoretical methods make predictions that can be interpreted quantitatively. For example, the ideal selectivity of H2 (CO2) from CH4 with a 25 μm thick IRMOF-1 film was experimentally measured as ~2.9 (0.65) whereas our predictions gave a selectivity of 3.1 (1.23) under the same conditions.

We now consider Matrimid/IRMOF-1 membranes using gas feeds containing 10% CO2 and 90% CH4 at a feed pressure of 2 atm at 35 °C. To describe this permeating mixture, the dual mode/partial immobilization model mentioned above was used. The parameters of this model were obtained by fitting the models to experimental data for Matrimid. This model predicts a CO2 selectivity of 38.1 for a Matrimid membrane under the conditions considered here. This differs somewhat from the experimental data of Perez et al., who reported a CO2 selectivity of 43.5 for pure Matrimid. The predictions of the Maxwell and Bruggeman models for this mixture are compared to the experimental data of Perez et al. in Fig. 3. The models agree with the experimental data in showing that the mixture selectivity of the membrane decreases as the IRMOF-1 content is increased. This can be understood from examining the predictions for a pure MOF membrane in Fig. 3, where our calculations for a defect-free membrane indicate IRMOF-1 is only weakly selective for CO2. The quantitative difference between our predicted results and the experimental data of Perez et al. for the MMMs appears to be almost entirely due to the discrepancy between the predictions of the model for the pure polymer and the experimental data.

*Fig. 3 Selectivity of CO2 from CO2/CH4 mixtures as a function of IRMOF-1 loading in Matrimid at a feed pressure of 2 atm and 35 °C. The feed gas composition is 10% CO2.*

### 3.2 Predicted performance of new MOF/Matrimid combinations for CO2/CH4 separations

The main outcome of the calculations described above is that the Maxwell and Bruggeman models show good agreement with all available experimental data for Matrimid/IRMOF-1 membranes. This suggests that a combination of various polymer/MOF membranes can be studied with these models to estimate the permeabilities of gas species in these mixed membranes prior to their fabrication. With this aim, we carried out similar calculations for Matrimid membranes with IRMOF-8, IRMOF-10, IRMOF-14 and CuBTC. These MOFs were studied as pure membranes using atomically detailed simulations in our earlier work, which indicated that these large pore MOFs have high permselectivities but low selectivities for CO2 and CH4 due to their large pore volumes.

Fig. 4 shows the Maxwell model predictions for ideal selectivity of CO2 from CH4 for mixed matrix membranes where the MOFs listed above are used as additives in Matrimid at a feed pressure of 2 atm and 35 °C. The trends of mixed matrix membranes with IRMOF-8, IRMOF-10, IRMOF-14 and CuBTC are very similar; the permeability of CO2 is improved relative to the pure polymer but the ideal selectivity is almost unchanged.

We have recently predicted that Cu(hfipbb)(H2hfipbb)0.5 has extremely high selectivity for membrane-based separation of CO2/CH4 mixtures using a combination of molecular dynamics, transition state theory and plane wave density functional theory calculations. Motivated by this result, we consider Matrimid/Cu(hfipbb)(H2hfipbb)0.5 mixed matrix membranes. The data for pure gas permeabilities of CO2 and CH4 in Matrimid was taken from the experimental work of Perez et al. for a feed pressure of 2 atm at 35 °C. We performed molecular simulations to calculate the permeability of CO2 in Cu(hfipbb)(H2hfipbb)0.5 at the same pressure and temperature. The diffusivity of CH4 in this MOF was too slow (<10^{-3} cm^2 s^{-1}) to be measured by molecular dynamics simulations, so we used transition state theory calculations to predict CH4 diffusion rate. The transition state theory
calculations, as explained in our previous work,\textsuperscript{5,6} gave a range rather than a precise value for the diffusivity of CH\textsubscript{4} in Cu(hfipbb)(H\textsubscript{2}hfipbb)\textsubscript{0.5}. The permeability of CH\textsubscript{4} in Matrimid/ Cu(hfipbb)(H\textsubscript{2}hfipbb)\textsubscript{0.5} membranes was calculated using both the upper and lower bounds on the CH\textsubscript{4} diffusivity in pure Cu(hfipbb)(H\textsubscript{2}hfipbb)\textsubscript{0.5}.

The Maxwell model predictions for Matrimid/Cu(hfipbb)(H\textsubscript{2}hfipbb)\textsubscript{0.5} mixed matrix membrane where the lower bound of the diffusivity of CH\textsubscript{4} in pure Cu(hfipbb)(H\textsubscript{2}hfipbb)\textsubscript{0.5} was used are shown in Fig. 4. Increasing the Cu(hfipbb)(H\textsubscript{2}hfipbb)\textsubscript{0.5} volume fraction from 0 to 30% increases the permeability of CO\textsubscript{2} from 9 to 20 Barrer. This result is similar to the effect of IRMOFs and CuBTC. In contrast to the other MOFs we studied, however, Cu(hfipbb)(H\textsubscript{2}hfipbb)\textsubscript{0.5} has a very high CO\textsubscript{2} selectivity as a pure MOF membrane due to the large difference between transport rates of CO\textsubscript{2} and CH\textsubscript{4}. As a result, a mixed matrix membrane of Matrimid/Cu(hfipbb)(H\textsubscript{2}hfipbb)\textsubscript{0.5} has an enhanced selectivity compared to pure Matrimid membrane. For example, Fig. 4 shows that a mixed matrix membrane with 30% Cu(hfipbb)(H\textsubscript{2}hfipbb)\textsubscript{0.5} has a selectivity for CO\textsubscript{2} of 95 while the selectivity of pure polymer membrane due to the large difference between transport rates of CO\textsubscript{2} and CH\textsubscript{4}. As a result, a mixed matrix membrane of Matrimid/Cu(hfipbb)(H\textsubscript{2}hfipbb)\textsubscript{0.5} has an enhanced selectivity compared to pure Matrimid membrane. For example, Fig. 4 shows that a mixed matrix membrane with 30% Cu(hfipbb)(H\textsubscript{2}hfipbb)\textsubscript{0.5} has a selectivity for CO\textsubscript{2} of 95 while the selectivity of pure polymer is 41. This figure also illustrates that 20% Cu(hfipbb)(H\textsubscript{2}hfipbb)\textsubscript{0.5} is enough to carry the mixed matrix membrane above the Robeson’s upper bound with a CO\textsubscript{2} selectivity of 72 and permeability of 15.7 Barrer.

Fig. 5 show the predictions of the Maxwell and Bruggeman models for ideal selectivity and permeability of CO\textsubscript{2} for Matrimid/Cu(hfipbb)(H\textsubscript{2}hfipbb)\textsubscript{0.5} membrane using both the upper and lower bounds of the CH\textsubscript{4} diffusivity in the MOF, respectively. The permeability of CO\textsubscript{2} in Cu(hfipbb)(H\textsubscript{2}hfipbb)\textsubscript{0.5} is almost 500 times higher than in Matrimid whereas the permeability of CH\textsubscript{4} in Cu(hfipbb)(H\textsubscript{2}hfipbb)\textsubscript{0.5} is very similar to ~10 times higher than Matrimid in Fig. 5a (5b). Therefore, as the volume fraction of Cu(hfipbb)(H\textsubscript{2}hfipbb)\textsubscript{0.5} in the MMM increases, both the ideal selectivity and permeability of CO\textsubscript{2} increase relative to pure Matrimid. This increase is, of course, less pronounced for the calculations carried out using the larger value for the diffusivity of CH\textsubscript{4} in Cu(hfipbb)(H\textsubscript{2}hfipbb)\textsubscript{0.5}. For example, the Maxwell model predicts a CO\textsubscript{2} ideal selectivity of ~55–168 (~44–59) as the volume fraction of Cu(hfipbb)(H\textsubscript{2}hfipbb)\textsubscript{0.5} changes from 0.1 to 0.5 when the lower (upper) bound on the CH\textsubscript{4} diffusivity is used. Most importantly, Fig. 5 demonstrates that using a MOF such as Cu(hfipbb)(H\textsubscript{2}hfipbb)\textsubscript{0.5} with high gas permeability and selectivity in a MMM can dramatically improve the membrane’s performance relative to pure polymer.

We also examined the ideal selectivity of H\textsubscript{2} from CH\textsubscript{4} and CO\textsubscript{2} for Matrimid/Cu(hfipbb)(H\textsubscript{2}hfipbb)\textsubscript{0.5} membranes. As shown in Fig. 6, the ideal selectivity of H\textsubscript{2} from CH\textsubscript{4} is high for Matrimid/Cu(hfipbb)(H\textsubscript{2}hfipbb)\textsubscript{0.5} membranes, similar to CO\textsubscript{2} separation from CH\textsubscript{4}. This result can be also explained by the significant difference in diffusion rates of CH\textsubscript{4} and H\textsubscript{2} in Cu(hfipbb)(H\textsubscript{2}hfipbb)\textsubscript{0.5}. The Maxwell model predicts an ideal selectivity for H\textsubscript{2} of ~450 for separation of H\textsubscript{2}/CH\textsubscript{4} mixtures with a mixed matrix membrane when the volume fraction of MOF is 0.5. This selectivity is 4 times higher than the H\textsubscript{2} selectivity of pure Matrimid. The ideal selectivity of CO\textsubscript{2} from H\textsubscript{2}, on
the other hand, is not very interesting because of the lack of difference in transport rates of these gas species in this MOF. The selectivity of CO$_2$ from H$_2$ with the pure Matrimid is $2.7^{[C24]}$ whereas it is less, $1.5^{[C24]}$, for a pure Cu(hfipbb)(H$_2$hfipbb)$_{0.5}$ membrane.

It is important to note that all of our calculations have considered gas mixtures that contain only dry gases. The development of practical membranes must also consider other species that are likely to be present, most notably water. IRMOFs are known to degrade under mild conditions in the presence of water, $^{[73]}$ a fact that would make them unsuitable for practical applications even if their properties for dry gas mixtures were attractive. It appears likely that Cu(hfipbb)(H$_2$hfipbb)$_{0.5}$ is far more stable with respect to water, although detailed durability experiments for this MOF have not yet been reported.

### 3.3 Selection of polymers for use in MOF-based MMMs

All of our results up to this point have been for MMMs in which Matrimid is the polymeric component. Our calculations predict that pairing a highly selective MOF, Cu(hfipbb)(H$_2$hfipbb)$_{0.5}$, with Matrimid can produce a MMM with attractive characteristics. We now turn our attention to another important aspect of developing MOF-based MMMs: what polymers can reap the largest advantages when used in combination with MOFs?

To address this question we just posed, we considered a series of hypothetical polymers that lie along the Robeson’s upper bound curve for CO$_2$/CH$_4$ separations. Specifying the position of a polymer along this line defines all the information needed to apply the Maxwell model to the polymer. For each hypothetical polymer, we used the Maxwell model for MMMs using IRMOF-1 or Cu(hfipbb)(H$_2$hfipbb)$_{0.5}$ as fillers. Our results are summarized in Fig. 7. Several well-known polymers are also shown on this figure.

The trends that are evident in Fig. 7 will be very useful in developing MOF-based MMMs. If the pure polymer membrane has a high selectivity for CO$_2$ but low permeability, adding a MOF can enhance the membrane’s permeability slightly with little or no change in the membrane’s selectivity. In this limit, the identity of the MOF appears to be unimportant.

Another extreme example of polymer performance is a polymer that is very permeable but has a little selectivity. As shown in Fig. 7, silicone rubber and PTMSP are examples of this kind. For these polymers, the identity of the MOF used in a MMM plays a critical role. A permeable but unselective MOF such as IRMOF-1 can yield a MMM with lower selectivity than the pure polymer. A highly selective MOF, in contrast, increases the selectivity of a MMM but slightly decreases the MMM’s CO$_2$ permeability.

Most importantly, Fig. 7 shows that there is a wide range of polymers that have moderate selectivity and moderate permeability for which adding an appropriate MOF can yield large performance enhancements. To realize these results, it is critical to use a highly selective MOF such as Cu(hfipbb)(H$_2$hfipbb)$_{0.5}$ rather than an unselective MOF such as IRMOF-1 or the other unselective MOFs examined in Fig. 4.

### Conclusion

Membrane-based separations have great potential for energy-efficient production of large volume chemicals. In this paper, we have used a combination of atomistic and continuum modeling to examine how polymeric membranes for gas separations can be enhanced by using metal organic framework materials to make composite films. Initial experiments indicate that it is relatively straightforward to fabricate high quality polymer/MOF
composites. Because of the very large number of MOFs that are known, development of this field requires methods to select polymer/MOF combinations that are well suited to specific separations of interest. Prior to the results we have reported here, no attempts to address this problem had been reported. We have previously focused on CO2/CH4 separations, but the combination of methods we have used is quite general and should create opportunities to rationally select polymer/MOF combinations for other industrially relevant separations.

Our work leads to several important conclusions. Most significantly, our models predict that polymer/MOF combinations exist that have permeability and selectivity that greatly exceed the pure polymer. Specifically, including Cu(hfip-bb)(H2hfipbb)0.5 particles in a Matrimid film was predicted to give composite membranes that exceed Robeson’s upper bound curve for CO2/CH4 separations. The very high selectivity of Cu(hfip-bb)(H2hfipbb)0.5 predicted by atomistic modeling for CO2 over CH4 is due to differences in the molecular diffusivities inside this MOF. Second, our calculations indicate that other (perhaps most) MOFs do not yield similar dramatic improvements in membrane performance. We showed that a series of well-known MOFs, including IRMOF-1 and CuBTC, can increase the permeability of CO2 through composite films relative to the pure polymer but do not improve membrane selectivity. This outcome is in agreement with initial experimental studies. It would of course be useful to extend our results to other MOFs that show large diffusion-based selectivities for CO2 and CH4. To date, however, Cu(hfip-bb)(H2hfipbb)0.5 is the only material that has been predicted to have this highly desirable property. The fact that a very large number of MOFs are known strongly suggests that many materials with similar properties exist. Efforts to identify these materials are likely to play an influential role in the development of this area.

Finally, our results illustrate the somewhat obvious point that a polymer/MOF composite with excellent properties for one gas separation may have less exciting properties for other gas separations. Specifically, Matrimid/Cu(hfip-bb)(H2hfipbb)0.5 films were seen to have excellent properties for CO2/CH4 and H2/CH4 separations, but mediocre properties for H2/CO2 separations. These conclusions all indicate that polymer/MOF composites have enormous potential in practical gas separation applications provided that methods such as those we have introduced are used to select good material combinations for the desired applications.

References