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Methodologies for screening and selection of crystalline microporous materials in mixture separations

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ABSTRACT
Ordered crystalline microporous materials such as zeolites, metal-organic frameworks (MOFs), and zeolitic imidazolate frameworks (ZIFs) offer considerable potential for separating a wide variety of mixtures. There are basically two different separation technologies that can be employed: (1) pressure swing adsorption (PSA) unit with a fixed bed of adsorbent particles, and (2) membrane device, wherein the mixture is allowed to permeate through thin micro-porous crystalline layers. The fundamental physico-chemical principles underlying the separations in these two devices are fundamentally different. In fixed bed adsorbers, diffusional effects are usually undesirable because these tend to produce distended breakthroughs and diminished productivities. For membrane separations, both intra-crystalline diffusion and mixture adsorption equilibrium determine permeation selectivities, and diffusion selectivities are often the primary drivers for separations.

Using Configurational-Bias Monte Carlo (CBMC) simulations of mixture adsorption equilibrium, and Molecular Dynamics (MD) simulations of guest diffusivities in a wide number of guest/host combinations, we demonstrate that adsorption and diffusion do not, in general, proceed hand-in-hand. Strong adsorption often implies lowered mobility. Consequently, the best material for use in fixed bed adsorbers does not always coincide with the ideal choice for use as thin layers in membrane devices. Methodologies for screening microporous materials for use in fixed-bed units and membrane devices are discussed using a large number of examples of industrially important separations.

1. Introduction

Ordered crystalline microporous materials such as zeolites (crystalline aluminosilicates), metal-organic frameworks (MOFs), and zeolitic imidazolate frameworks (ZIFs) offer potential for separation of a wide variety of mixtures: CO₂/CH₄, CO₂/N₂, CO₂/H₂, CH₄/H₂, CH₄/N₂, CO₂/CO/CH₄, CO₂/C₂H₆, CO₂/C₃H₈, O₂/N₂, Xe/Kr, fluorocarbons, alkane/alkene, alkyne/alkene, butane isomers, alkane isomers, xylene isomers, benzene/cyclohexane, and ethylbenzene/styrene [1–35]. Particularly potent in many separations are MOFs with exposed M²⁺ cation sites such as M₂(dobdc) [M = Mg, Mn, Co, Ni, Zn, Fe; dobdc⁴⁻ = 2,5-dioxo-1,4-benzenedicarboxylate]; these MOFs are also referred to as M-MOF-74 and CPO-27-M (see framework in Fig. 1). M-MOF-74 has one-dimensional (1D) hexagonal-shaped channels of approximately 11 Å. Another important MOF with exposed cation sites is M₃(BTC)₂ [M = Cu, Cr, Mo; BTC⁴⁻ = 1,3,5-benzenetricarboxylate]; Cu₃(BTC)₂ is also known as HKUST-1. In ZIFs, the Zn or Co atoms are linked through N atoms of ditopic imidazolates to form a range of neutral framework structures. The frameworks of ZIF compounds can be represented by M(IM)₂ [M = tetrahedrally coordinated metal atom; IM = imidazolate and its derivative], similar to that of (AlO₂)ₓ(SiO₂)ₓ zeolites. The M-M angle of 145° is close to the Si–O–Si angle typically found in zeolites. ZIF-8, for example, has the structural topology of SOD (sodalite), and consists of cages separated by narrow windows of 3.3 Å size.

In comparison to traditionally used porous materials such as zeolites, MOFs offer significantly higher surface areas and porosities. The structural details and pore landscapes of all the zeolites and MOFs considered in this MOF are provided in the Supplementary material accompanying this publication. As illustration, Fig. 2 presents data for surface areas, pore volumes, framework densities, and characteristic pore dimensions of some representative adsorbents. The commonly known MFI zeolite, for example, has a channel dimension of 5.5 Å, pore volume of 0.165 cm³ g⁻¹, and surface area of 490 m² g⁻¹. Significantly higher surface areas are available with MOFs; for example MOF-177 has a surface area of 4800 m² g⁻¹. The accessible pore volumes of MOFs are commonly in the 0.5–2 cm³ g⁻¹ range. For any given separation application, there is a need to identify the microporous material with the ideal pore size, and surface area that offers the right degree of interactions (van der Waals, electrostatic, π-electron exchange) with the guest molecules.

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In practice, separations using zeolites, MOFs and ZIFs are conducted in either pressure swing adsorption (PSA) units consisting of fixed beds packed with adsorbent, or membrane permeation devices that consist of thin microporous crystalline layers, typically a few micrometers in thickness. PSA units are operated in a cyclical manner, with adsorption and desorption cycles [13,14,36–39]. Most commonly, the separation performance in a fixed-bed adsorber is dictated by mixture adsorption equilibrium. The separation effectiveness of fixed-bed devices is dictated by a combination of adsorption selectivity and uptake capacities. For separation of a binary mixture of components A and B, the adsorption selectivity is defined by

\[ S_{\text{ads}} = \frac{q_A}{q_B} \]

where the \( q_A \) and \( q_B \) represent the molar loadings within the zeolite or MOF that is in equilibrium with a bulk fluid mixture with mole fractions.

**Fig. 1.** M-MOF-74 has 1D hexagonal-shaped channels of 11 Å size.

**2,5- dioxido-1,4-benzenedicarboxylate = dobdc**

\[ \text{M}_2(\text{dobdc}) \]

\[ \text{M} = \text{Mg, Fe, Co, Ni} \]

\[ 11 \text{ Å hexagonal channels} \]

**Fig. 1.** M-MOF-74 has 1D hexagonal-shaped channels of 11 Å size.

**Fig. 2.** Comparison of surface area, pore volumes, framework densities, and characteristic dimensions of some representative zeolites, MOFs and ZIFs.
A, and \( y_B = 1 - y_A \). The molar loadings, also called gravimetric uptake capacities, are usually expressed with the units \( \text{mol kg}^{-1} \). The volumetric uptake capacities are

\[
Q_A = \rho A Q A, Q B = \rho B Q B \tag{2}
\]

where \( \rho \) is the crystal framework density of the zeolite or MOF, expressed in units of \( \text{kg m}^{-3} \) or \( \text{g L}^{-1} \). The selectivity \( S_{ads} \) may be calculated on the basis of experimental data on unary isotherms, along with the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz [40] for mixture adsorption equilibrium.

High uptake capacities are desirable because these result in longer breakthrough times, and reduced frequency of bed regeneration. Higher values of \( S_{ads} \) are desired because they lead to sharper breakthrough fronts and larger differences between the breakthrough times of individual constituents. If high product purities are desired, then this also demands \( S_{ads} > 1 \). Most commonly, however, high uptake capacities do not go hand-in-hand with high selectivities [13,14].

For membrane separations, both adsorption equilibrium, and intra-crystalline diffusion determine membrane permeation selectivities

\[
S_{perm} = \frac{N_A / f_A}{N_B / f_B} \tag{3}
\]

In Eq. (3), \( N_A \) and \( N_B \) are the permeation fluxes; \( f_A \) and \( f_B \) are the partial fugacities in the upstream compartment. The permeation selectivity can be expressed as

\[
S_{perm} = S_{ads} \times S_{diff} \tag{4}
\]

where \( S_{diff} \) is the diffusion selectivity that can be taken, as a good approximation, equal to the ratio of the self-diffusivities \( D_{i,self} \) in the mixture [15,41]

\[
S_{diff} = \frac{D_{1,self}}{D_{2,self}} \tag{5}
\]

To set the scene, and define the objectives of this review article, let us consider the separation of \( \text{CO}_2 \) from \( \text{CH}_4 \) that is relevant to the purification of natural gas, which can contain up to 92% \( \text{CO}_2 \) impurity at its source [42]. Removal of \( \text{CO}_2 \), which is most commonly accomplished using amines, is conducted at pressures ranging between 2 MPa and 7 MPa [43]. The separation requirements for production of liquefied natural gas (LNG) are rather stringent, often requiring the achievement of impurity levels of less than 500 ppm \( \text{CO}_2 \). Fig. 3a provides a comparison of \( \text{CO}_2/\text{CH}_4 \) adsorption selectivities \( S_{ads} \) and \( \text{CO}_2/\text{CH}_4 \) diffusion selectivities \( S_{diff} \) for 50/50 \( \text{CO}_2/\text{CH}_4 \) mixtures for selected zeolites and MOFs at a total fugacity \( f_t = 1 \text{ MPa} \), and temperature \( T = 300 \text{ K} \). The data on \( S_{ads} \) are collected from earlier published material [15,16,41,44,45]. The symbols marked blue are cage-type structures with narrow windows. (b) Comparison of CBMC data with IAST estimations of the component loadings for adsorption of 50/50 \( \text{CO}_2/\text{CH}_4 \) mixtures in \( \text{NaY} \) zeolite at 300 K.
For most adsorbents, the CBMC simulations of component loadings in the mixture are in good agreement with the IAST estimations, based on CBMC simulations of unary isotherms. As illustration, Fig. 3b compares CBMC data with IAST estimations for NaY zeolite; the agreement between the CBMC data and IAST estimates is very good. There are, however, instances of some quantitative failures of the IAST for cases of segregated adsorption caused by preferential location of CO₂ molecules at window regions of cage-type zeolites [47,48].

There appear to be two fundamentally different categories of behaviors in Fig. 3a. The adsorption and diffusion selectivities of CH₄, DDR, ERI, ITQ-29, ZIF-8, and TSC (indicated in blue) serve to complement each other; we obtain $S_{ads} > 1$ and $S_{diff} > 1$. These materials have cage-type topologies in which adjacent cages are separated by narrow windows in the 3.3 Å–4.3 Å size range; see Supplementary material for pore landscapes of CH₄, DDR, TSC, ERI, ITQ-29, and ZIF-8. In all such structures, CO₂ jumps length-wise across the narrow windows as evidenced in video animations [49,50]. Since the cross-sectional dimension of CO₂ is smaller than that of CH₄, this accounts for the significantly higher diffusion selectivities in favor of CO₂.

In the second category of materials (indicated by black symbols in Fig. 3a) there is lack of synergy between adsorption and diffusion, i.e. we find $S_{ads} > 1$ but $S_{diff} < 1$, i.e. the diffusion selectivity favors the more poorly adsorbing CH₄; these materials fall into four sub-classes of materials, in all of which the channel dimensions are larger than about 5 Å.

- One-dimensional (1D) channels (e.g. TON, LTL, MTW, MgMOF-74, MIL-53)
- 1D channels with side pockets (e.g. FER, MOR)
- Intersecting channels (e.g. MFI, BEA, ISV, Zn(bdc)daibo)
- “Open” structures with large cavities (e.g. NaY, NaX, IRMOF-1, CuBTC, MOF-177)

The question arises: In these four topologies, why is the diffusion selectivity in favor of CH₄ that has the larger kinetic diameter? Another interesting observation is that the hierarchy of CO₂/CH₄ diffusion selectivities $S_{diff}$: FAU (= all-silica Faujasite) > NaY > NaX. These three materials have the same pore size and topology; the structure has cavities that are about 11 Å in size. Adjacent cavities are separated by 10-ring windows of 7.3 Å size; the window aperture does not offer significant free-energy barriers for inter-cage hopping. The only differences reside in the Si/Al ratio, and the number of extra-framework Na⁺ cations; for each unit cell (uc) of these materials, we have FAU (192 Si, 0 Al, 0 Na⁺, Si/Al = ∞); NaY (138 Si, 54 Al, 54 Na⁺, Si/Al = 2.56); NaX (106 Si, 86 Al, 86 Na⁺, Si/Al = 1.23). Clearly, the diffusion characteristics are determined by factors other than pore size and guest confinement. Particularly noteworthy is the fact that NaX zeolite, commonly known by its trade name 13X, has the highest adsorption selectivity, but the lowest diffusion selectivity. What is the rationalization for this strong dependence of the diffusion selectivity on the Si/Al ratio, in disfavor of CO₂?

What screening criteria should we use to select the best material for use in fixed bed adsorbers? How do we conduct the analogous screening and selection of materials for use as thin layers in membrane permeation units?

The primary objective of this article is to address the set of four questions posed above, and obtain answers that will help in the choice of the ideal material for a given separation task. For illustration of the suggested methodology for screening, we undertake detailed analyses of a wide number of different separations that are of importance in the process industries.

2. CO₂/CH₄ mixture separations

Fig. 4a, b present MD simulation data on the loading dependence of the self-diffusivities of CO₂ and CH₄ in FAU, NaY, and NaX. The self-
Fig. 5. Zero-loading diffusivities $D_{i}(0)$ of light gases in (a) AFI, (b) MgMOF-74, (c) MFI, (d) CuBTC, (e) MOF-177, and (f) IRMOF-1, plotted as a function of the corresponding values of the isosteric heats of adsorption, $Q_{st}$. These data are based on CBMC and MD simulations, reported in earlier works [41,45,122].


Fig. 6. (a) Experimental data of Remy et al. [52] for transient breakthrough of equimolar CO2/CH4 mixtures through fixed bed adsorber packed with MgMOF-74 operating at 308 K. The dotted lines represent the shock-wave model for breakthroughs. (b) Plot of the separation potential, ΔQ, calculated using the formula ΔQ versus the volumetric CO2 uptake capacity for 50/50 CO2/CH4 mixture separations in different zeolites, and MOFs. (c) Robeson plot for separation of CO2/CH4 mixtures; the permeation selectivities, Sperm, for different microporous materials are plotted against the CO2 permeability.

diffusivity of CO2 strongly decreases as the number of extra-framework cations increases, whereas the self-diffusivity of CH4 is practically the same in the three materials. Due to strong electrostatic interactions, the binding strength of CO2 increases with increasing number of Na+ cations. The isosteric heats of adsorption, Qst, are an appropriate measure of the binding strength and can be determined from CBMC simulations using fluctuation formula as described in earlier works [41,45]. In Fig. 4c, the zero-loading diffusivities Δi(0) of CO2 in FAU, NaY (54 Na+/uc), and NaX (86 Na+/uc) zeolites are plotted against the corresponding values of the Qst, extrapolated to zero-loads; the stronger the binding, the lower the diffusivity. The data in Fig. 4 rationalizes the hierarchy of CO2/CH4 diffusion selectivities Δdiff: FAU > NaY > NaX.

Plots of zero-loading diffusivities Δi(0) of light gases (H2, N2, CH4, CO2, He, Ne, Kr) versus the corresponding values of the isosteric heats of adsorption Qst are shown in Fig. 5 for AFI, MgMOF-74, MFI, CuBTC, MOF-177, and IRMOF-1. The values of Qst were determined from CBMC simulations in each of these materials, the strongest binding is with CO2; this explains why the CO2/CH4 diffusion selectivities are lower than unity in all these six materials (cf. Fig. 3a). Of these six materials examined in Fig. 5, we also note that the Qst value for CO2 in MgMOF-74 is the highest, indicating strong CO2 binding. Neutron diffraction data [51] establish that CO2 molecules attach strongly via O atoms to the unsaturated Mg2+ atoms of MgMOF-74 (see Fig. 1); this strong binding accounts for the high adsorption selectivity of CO2 (cf. Fig. 3a). For effective use of the three materials with the highest values of Qst, i.e. NaX, NaY, and MgMOF-74, in PSA units, the crystal size must be chosen to be small enough to minimize the negative influence of intra-crystalline diffusional resistances. Adsorbent materials suitable for use in fixed bed adsorbers are usually those with characteristic pore dimensions larger than about 6 Å; the Supplementary material contains information on pore sizes of all of the host structures discussed in this article. The experimental data of Remy et al. [52] for transient breakthroughs of CO2/CH4 mixtures through a fixed bed adsorber packed with MgMOF-74 are shown in Fig. 6a. There is a slight distention in the breakthrough characteristics; this distention is undesirable because it leads to diminished productivities of purified CH4 that is recovered during the time interval Δt. The maximum achievable productivity of pure CH4 is realized when both intra-crystalline diffusion and axial dispersion effects are completely absent and the concentrations “fronts” of the fluid mixture traverse the fixed bed in the form of shock waves [14,53]. The shock-wave model solution is indicated by the dotted lines in Fig. 6a. For a binary mixture with mole fractions yA, and yB, in the feed mixture, the maximum achievable productivity, ΔQ, can be calculated using the shock-wave model; the result is [14]

\[
\Delta Q = Q_A \left( y_B \frac{y_A}{1-y_B} - Q_B \right)
\]

The physical significance of ΔQ, conveniently expressed in the units of mol per L of adsorbent, is that it represents the maximum amount of pure component B (less strongly adsorbed component) that can be recovered during the adsorption phase of fixed bed separations. The quantity ΔQ is an appropriate combination of selectivity and uptake capacity that is reflective of the separation potential of separations in fixed beds packed with a specific adsorbent [14]. The quantity ΔQ is distinctly different from the working capacity, whose evaluation requires us to additionally specify the regeneration strategy. Using the CBMC data on mixture adsorption equilibrium (cf. Fig. 3), Fig. 6b plots the
separation potential, $\Delta Q$, versus the volumetric CO$_2$ uptake capacity for different materials. Based on this screening methodology, the three best materials to use in PSA units are MgMOF-74, NaX, and NaY. Other factors such as framework stability, resistance to moisture in the feed, material and regeneration costs, need to be taken into consideration in the final choice of adsorbent; discussions on these factors are beyond the scope of this article.

For use of the materials in membrane constructs, the screening needs to be done differently because the membrane performance is strongly influenced, often dominated, by diffusional influences. In the literature the performance of membranes is judged on the basis of the Robeson plot [54] of the permeation selectivity $S_{\text{perm}} = S_{\text{ads}} \times S_{\text{diff}}$ versus the CO$_2$ permeability of the membrane, $\Pi_i$, defined by

$$\Pi_i = \frac{N_i}{\Delta f_i / \delta}$$

(7)

where $\delta$ is the thickness of the crystalline layer on the membrane; $\Delta f_i = f_i - f_0$ is the difference in the partial fugacities in the bulk fluid mixtures in the upstream ($z = 0$) and downstream ($z = \delta$) compartments. If the downstream conditions are such that the loadings are negligibly small, the CO$_2$ permeability can be determined from MD simulations by using the following expression [15]

$$\Pi_i = \frac{\rho D_{\text{int}} q_i}{f_i}$$

(8)

Fig. 6c presents the Robeson plot for CO$_2$/CH$_4$ mixture separation in the various microporous structures, for an upstream membrane fugacity.

Fig. 7. (a) Comparison of diffusion selectivities, $S_{\text{diff}}$, and adsorption selectivities, $S_{\text{ads}}$ for 15/85 CO$_2$/N$_2$ mixtures. The conditions correspond to $f_0 = 1$ MPa and 300 K. (b) Plot of the separation potential, $\Delta Q$, versus the volumetric CO$_2$ uptake capacity for 15/85 CO$_2$/N$_2$ mixture separations in different zeolites, and MOFs. (c) Robeson plot for separation of CO$_2$/N$_2$ mixtures; the permeation selectivities, $S_{\text{perm}}$, for different microporous materials are plotted against the CO$_2$ permeability. The plotted data are culled from earlier published works [15,16,41,44,45].
The highest permeation selectivities for CO₂/CH₄ separation with $S_{\text{perm}} > 100$ are obtained with zeolites with 8-ring windows such as DDR, CHA, and ERI; in these cases $S_{\text{ads}}$ and $S_{\text{diff}}$ complement each other. For DDR and CHA, there is experimental evidence that such high permeation selectivities can be realized in practice [47,55–61]. For MFI, the $S_{\text{perm}}$ value of 2.3 is in agreement with experiment [58]. Open, large pore, structures such as MOF-177, CuBTC have high $\Pi_i$ but low $S_{\text{perm}}$. On the other hand, ERI, DDR, and CHA have significantly higher $S_{\text{perm}}$ values but with lower $\Pi_i$. High values of $S_{\text{perm}}$ rarely go hand in hand with high $\Pi_i$. For technological applications, a compromise has to be made. The compromise structure could perhaps be NaY with reasonably high permeability and permeation selectivity. There is considerable scope for development of novel materials that would lead to a performance at the top right corner of the Robeson plot, using mixed-matrix membranes that attempts to profit from both adsorption and diffusion characteristics of the constituent materials.

3. CO₂/N₂ mixture separations

The capture of CO₂ from flue gases emanating from power plants involves separation of 15/85 CO₂/N₂ mixtures [6,18]. Due to its lower polarizability and quadrupole moment, the adsorption strength of N₂ is lower than that of CO₂ in all materials; therefore, the adsorption selectivity $S_{\text{ads}} > 10$ in all adsorbents. The smaller molecular dimensions of N₂, coupled with its poor adsorption strength, ensures that the CO₂ diffusivity is lower than that of N₂ in all materials. Fig. 7a presents a comparison of diffusion selectivities, $S_{\text{diff}}$, and adsorption selectivities,
S_{ads} for 15/85 CO_{2}/N_{2} mixtures. The highest adsorption selectivities are realized with NaX zeolite. As with CO_{2}/CH_{4} mixtures, the hierarchy FAU > NaY > NaX holds for CO_{2}/N_{2} diffusion selectivities for the same reasons as elucidated in the foregoing section. For use in fixed bed units, screening on the basis of the plot of \Delta Q versus volumetric CO_{2} uptake capacity leads to the hierarchy MgMOF-74 > NaX > NaY; see Fig. 7b. The superior performance of MgMOF-74 is primarily due to its higher CO_{2} uptake capacity. However, Pirngruber et al. [62] argue that the material with the strongest affinity for CO_{2} is not necessarily the best adsorbent because of the difficulty of regeneration.

For selection of materials for use in membrane devices, the Robeson plot is presented in Fig. 7c. The S_{perm} estimate for MFI of 8.2 is in reasonable agreement with the experiments of Bernal et al. [63]. The best combination of S_{perm} and \Pi_{i} values are obtained with NaX, NaY, and MgMOF-74. There is experimental evidence that the predicted permeation selectivities for NaY can indeed be realized in practice [64–67].

4. CO_{2}/H_{2} mixture separations

The separation of CO_{2}/H_{2} mixtures is important in the context of H_{2} purification and H_{2} production processes that are commonly operated at high pressures [42,68,69]. Due to its smaller molecular dimensions, and lower adsorption strength the diffusion selectivity favors H_{2} whereas the adsorption selectivity favors CO_{2}; see Fig. 8a. The highest H_{2}/CO_{2} diffusion selectivity is with ZIF-8, whereas the highest CO_{2}/H_{2}
adsorption selectivity is exhibited by NaX zeolite. For CO₂/H₂ separations in fixed bed units for production of pure H₂, screening on the basis of the plot of ΔQ versus volumetric CO₂ uptake capacity leads to the hierarchy MgMOF-74 > NaX > NaY; see Fig. 8b; this hierarchy is precisely the same as for CO₂/CH₄ and CO₂/N₂ mixtures.

For screening materials for use in membrane devices, the Robeson plot is presented in Fig. 8c. The best materials for CO₂-selective membrane operations are NaX, NaY, and MgMOF-74 that lie in the top right corner. For H₂-selective membrane operations, ZIF-8 is the suitable choice. There is recent experimental evidence in the literature to show that H₂-selective separation is possible with ZIF-7 and ZIF-8 membranes [70,71]. The H₂/CO₂ permeation selectivity value for ZIF-8 reported by Zhang et al. [71] is 4.6, in reasonably good agreement with the predictions based on molecular simulations as presented in Fig. 8c.

5. CH₄/H₂ mixture separations

The separation of CH₄/H₂ mixtures is important in the context of H₂...
purification, recovery, and production processes [42,68,69]. In all materials, the diffusion selectivity favors H2 whereas the adsorption selectivity favors CH4; see Fig. 9a. The highest H2/CH4 diffusion selectivity is with ITQ-29 and CHA, whereas the highest CH4/H2 adsorption selectivity is exhibited by NaX zeolite. For separations in fixed bed units for production of pure H2, screening on the basis of the plot of ∆Q versus volumetric CH4 uptake capacity leads to the hierarchy NaX > MgMOF-74 > MFI > NaY; see Fig. 9b.

For screening materials for use in membrane devices, the Robeson plot is presented in Fig. 9c. The best materials for CH4-selective membrane operations, suitable choices are Mg2(dobdc) [18], 13X zeolite [6,18], mmen-CuBTTri (formed by the incorporation of the incorporation of N,N-dimethylhexylenediamine (mmen) into H2(CuCl)3(BTTri)6 (CuBTTri; H3BTTri = 1,3,5-tri(1H-1,2,3-triazol-4-yl)benzene) [82], mmen-Mg2(dobdc) ([dobdc]4− = 4,4′-dioxido-3,3′-biphenyldicarboxylate) [81], SIFSIX-3-Cu [based on pyrazine/copper(II) two-dimensional periodic 4× square grids pillared by silicon hexafluoride anions] [83], and SIFSIX-3-Zn [83].

![Fig. 11.](image)

6. Screening materials for CO2 capture on the basis of experimental data on unary isotherms

An important conclusion to be drawn from the screening of materials for CO2 capture in fixed bed operations is that the material possessing the highest potential for production of pure CH4 (cf. Fig. 6b), N2 (cf. Fig. 7b), or H2 (cf. Fig. 8b) is not the one that possesses the highest adsorption selectivity (i.e. NaX zeolite), but MgMOF-74 that has the right combination of selectivity and uptake capacity. This is an important conclusion that needs to be validated on the basis of experimental data. Towards this end, we compare the separation potentials ∆Q using calculations based on the IAST model, along with experimental data on the unary isotherms of CO2, CH4, N2, and H2. For 50/50 CO2/CH4 mixtures at a total of 600 kPa, the plot of ∆Q versus volumetric CO2 uptake capacity is presented in Fig. 10a. The three best materials are NiMOF-74, MgMOF-74 and 13X zeolite, in agreement with the screening results using molecular simulations presented in Fig. 6b. The screening results for 15/85 CO2/N2 mixture separations at total pressure of 100 kPa are shown in Fig. 10b. The obtained hierarchy of ∆Q values: MgMOF-74 > NiMOF-74 > 13X, is the same as that in Fig. 7b, deduced on the basis of molecular simulations. The screening results for 20/80 CO2/H2 mixture separations at total pressure of 6 MPa are shown in Fig. 10c. In this case, the hierarchy of ∆Q values is: MgMOF-74 > CuTDPAT > 13X, agreeing with the corresponding hierarchy in Fig. 8b while noting that there are no molecular simulation results available for CuTDPAT [69]. The reliability of molecular simulation data for screening materials, especially zeolites, for CO2 capture applications is due to the fact that the force fields for CO2, CH4, N2, and H2 used in the simulations have been developed on the basis of extensive experimental data on unary isotherms [72,73]. For MOFs and ZIFs, the generic UFF [74] and DREIDING [75] force fields were used; consequently the results are somewhat less reliable, especially for host materials with open metal sites.

For industrial production of pure H2, steam-methane reformer off-gas, after it has been further treated in a water-gas shift reactor, is a commonly used feed gas stream, with typical compositions 70–80% H2, 15–25% CO2, 3–6% CH4, and 1–3% CO [76–78]. For most adsorbents, the sequence of breakthroughs in fixed bed adsorbers follows the increasing hierarchy of adsorption strengths, i.e. H2, CH4, CO, and CO2. This implies that the CH4/H2, and CO/H2 adsorption selectivities are far more relevant than the CO2/H2 selectivity. The precise definition of selectivity to be used for multicomponent gas mixtures that are relevant to fixed bed operations is ambiguous. In this case, the proper metric is the separation potential quantifying the maximum achievable productivity of pure H2 is derived from the shock-wave model [14]

\[
\Delta Q = \left( Q_{\text{H2}} + Q_{\text{CO}} + Q_{\text{CO2}} \right) \frac{y_{\text{H2}}}{1-y_{\text{H2}}} - Q_{\text{H2}}
\]

(9)

Fig. 10d presents plot of ∆Q vs volumetric uptake capacity for four different adsorbents. The best MOF for this separation task is CuBTC; this is because CO2/H2 selectivity is largely irrelevant for H2 production processes even though CO2 may be the present as the largest impurity in the feed mixture.

7. CO2 capture from ambient air

The majority of research on CO2 capture with MOFs has its focus on flue gas mixtures that typically contain 15% CO2, and 85% N2.
More recently, the potential of MOFs for CO₂ capture from ambient air has been the subject of a number of investigations [79–83]. Typically, the CO₂ concentrations in ambient air are about 400 ppm (=0.04%). Higher CO₂ concentrations, up to about 0.5%, are encountered in confined spaces such as in aeroplanes, submarines, space vehicles, and inside space suits of astronauts [84]. There is anecdotal evidence of curtailment of a space walk due to increase of CO₂ levels inside a space suit, that uses canisters containing lithium hydroxide for CO₂ capture [85].

Fig. 11a presents a plot of the adsorption selectivity versus volumetric CO₂ uptake capacity for CO₂/N₂ mixtures containing 400 ppm CO₂; the objective of the separation task is to produce N₂ containing less than 40 ppm CO₂. All six materials have selectivity values exceeding 100; the highest selectivity is achieved with mmen-Mg₂(dopbdc) [81]. There are, however, large differences in the CO₂ uptake capacities, ranging from 0.023 mol L⁻¹ for 13X zeolite to 1.6 mol L⁻¹ for mmen-Mg₂(dopbdc) [81], and SIFSIX-3-Cu [83]. The maximum productivity of pure N₂ (< 40 ppm CO₂) may be determined for each MOF using Eq. (6). The two best performing MOFs are mmen-Mg₂(dopbdc) and SIFSIX-3-Cu, that have both high uptake capacities; see Fig. 11b.

8. Alkene/alkane, and alkyne/alkene separations

There are stringent purity constraints of > 99.95% on C₂H₄ and C₃H₆ used as feedstocks to polymerization reactors. In order to meet required purity levels, distillation columns in currently used technologies for C₂H₄/C₂H₆ and C₃H₆/C₃H₈ separations need to operate at high pressures and cryogenic temperatures, employing high reflux ratios. The alkene/alkane distillation units are some of the largest and tallest distillation columns used in the petrochemical industries. Consequently, there is considerable economic incentive for development of energy efficient alternatives. One technological option is to employ a hybrid distillation-membrane scheme such as the one pictured in Fig. 12. Based on literature information, ZIF-8 membranes have potential applications for separation of both C₂H₄/C₂H₆, and C₃H₆/ C₃H₈ mixtures [86–88]. The separations using ZIF-8 membranes is primarily based on differences in the diffusivities of the alkenes and alkanes; such differences arise due to subtle differences in bond lengths and bond angles [41]. The adsorption selectivities for C₂H₄/C₂H₆, and C₃H₆/ C₃H₈ mixtures using ZIF-8 favor the saturated alkane [37,86,89]; this implies that adsorption and diffusion do not proceed hand in hand. The diffusion selectivities over-ride the adsorption selectivities, yielding permeation selectivities in favor of the unsaturated alkene [37,86]. The experiments of Bux et al. [86] for a ZIF-8 membrane show that the C₂H₄/C₂H₆ permeation selectivity is in the range of 2–3. For C₃H₆/C₃H₈ permeation across ZIF-8 membrane, the permeation selectivities, Sperm, reported in the experiments of Pan et al. [87] and Liu et al. [88] show values in the range of 30–35. These permeation selectivity values are significantly higher than the relative volatility of 1.14 for C₃H₆/C₃H₈; consequently, the hybrid process can be expected to have superior separation capability when compared to distillation alone. Importantly, the hybrid scheme in Fig. 12 contributes to alleviating the load on the condensers and reboilers.
For C2H4/C2H6, and C3H6/C3H8 separations in fixed-bed adsorption devices, a vast majority of the MOFs reported in the literature selectively adsorb the unsaturated alkenes [1–3,90]; see the plots of selectivity vs alkene uptake capacity for a few selected MOFs in Fig. 13a,b. Simultaneous and cooperative hydrogen-bonding, and π⋯π stacking interactions account for the stronger binding of C2H4 in NOTT-300. The π-complexation of the alkenes with Ag (I) ions of PAF-1-SO3Ag, account for its high C2H4/C2H6 selectivity. Cadiau et al.[91] report the synthesis of NbOFFIVE-1-Ni (=KAUST-7), whose effective aperture permits ingress of the C3H6 molecules, but practically excludes C3H8 on the basis of subtle differences in bond lengths and bond angles.

The separation capability of M-MOF-74 [M = Mg, Mn, Co, Ni, Zn, Fe] has been established in laboratory studies[3,90]; C2H4, and C3H6 can selective bind with M2+ of M-MOF-74, with side-on attachment and π-coordination [3]. Mukherjee et al.[12] also show that π-complexation triggered Lewis acid–base interactions between the open metal sites of M-MOF-74 and the π-electron rich benzene molecules can be exploited to achieve benzene/cyclohexane separations with high selectivities towards benzene; see Figs. S94 and S95 of Supplementary material for further details.

An important point to note is that the desired pure alkene can only be recovered during the desorption phase [3] of PSA operations. Using the shock-wave model, the maximum productivity of the more strongly adsorbed alkene (component A) is given by [14].
The plots of the separation potential versus the alkene uptake capacity for 50/50 C2H4/C2H6, and 50/50 C3H6/C3H8 mixtures are presented in Fig. 13c,d. It is interesting to note that the MOFs with the highest selectivities, NOTT-30 and KAUST-7, are not the ones displaying the highest productivity for production of pure alkene. For both mixtures, M-MOF-74 (M = Fe, Mn, Co, Ni) yield the best separations.

There are, however, practical technological issues associated with achieving the required > 99.95% purities in PSA units in the desorption phase. It becomes necessary to operate with multiple beds involving five different steps; the alkene product of the desired purity is recovered in the final step by counter-current vacuum blowdown [92,93]. Purely from a technological viewpoint, it is preferable to use adsorbents that are selective to the saturated alkanes, so that the desired alkenes are recoverable in the adsorption cycle [94]. The preferential adsorption of alkanes is only possible if separations are based on van der Waals interactions alone. However, the adsorption selectivities cannot be expected to be high. Indeed, computational screening of 300000 all-silica zeolite structures by Kim et al. [95] results in the discovery of SOF zeolite, that has a C2H6/C2H4 selectivity of only 2.9. This selectivity value of 2.9 can be matched by ZIF-7 [94,96], and ZIF-8 [89]. Two recent publications, also report ethane-selective adsorption with Ni (bdc)(ted)0.5 [97] and PCN-250 [98] but our IAST estimates of the adsorption selectivities at 298 K yield values close to 2; this value is too low for achievement of the desired purity levels.

The C2H4 and C3H6 feedstocks to the polymerization reactors are also subject to strict constraints on the presence of the corresponding alkynes, C2H2 (ethyne) and C3H4 (propyne). Typically, the alkyn content of alkylene/alkene feed mixtures is 1%. The presence of alkyn impurities higher than 40 ppm may poison the polymerization catalyst and have a deleterious effect on the polymer product. Current technologies for separation of C2H2/C2H4 and C3H4/C3H6 use absorption in dimethyl formamide (DMF); solvent regeneration is energy consuming. There is considerable research effort expended in recent years on the development of MOFs for this separation task [5,24–28,31,99]. Fig. 14 presents a plot of the separation potential ΔQ versus the volumetric uptake capacity of C2H2 for separation of 1/99 C2H2/C2H4 mixtures using SIFSIX-(1-Cu, 2-Cu, 3-Zn, 2-Cu-i, 3-Ni, 14-Cu-i), M’MOF-3a, and UTSA-100a. The total pressure, p = 100 kPa, and temperature T = 298 K. The unary isotherm data for other MOFs are from the published literature [13,14,100].
We shall examine whether significant improvements in separation performance can be achieved by use of other materials. To meet this objective, we perform IAST calculations of mixture adsorption equilibrium. Fig. 15a presents a plot of the adsorption selectivity vs volumetric uptake capacity of C₃H₆ for separation of 30/70 C₃H₆/N₂ mixtures using M-MOF-74 (M = Fe, Ni, Mg, Zn), 13X zeolite, and Fe-MIL-100. The highest selectivity is achieved with Fe-MOF-74, whereas the highest volumetric uptake capacity of C₃H₆ is with NiMOF-74. The desired product C₃H₆ can be recovered in the desorption phase; the maximum productivity of each MOF, calculated using Eq. (10), is presented in Fig. 15b as a function of the volumetric uptake capacity of C₃H₆. The best separation potential is offered by NiMOF-74 that has the highest uptake capacity for C₃H₆. It is also interesting to note that lowest productivity of pure C₃H₆ is with Fe-MIL-100, whose productivity is even lower than that of the commercially available 13X zeolite.

10. Separation of mixtures of hexane isomers

The separation of hexane isomers is required for production of high-octane gasoline. The values of the Research Octane Number (RON) increases with the degree of branching; the RON values are: n-hexane (nC₆) = 30, 2-methylpentane (2MP) = 74.5, 3-methylpentane (3MP) = 75.5, 2,2 dimethylbutane (22DMB) = 94, and 2,3 dimethylbutane (23DMB) = 105. The di-branched isomers are therefore the preferred products for incorporation into the high-octane gasoline pool [7,37,103]. Currently, the separation of hexane isomers is performed using LTA-5A zeolite that operates on the principle of molecular sieving; see the process flow diagram in Fig. 16a. Linear nC₆ can hop from one cage to the adjacent cage through the 4 Å windows of LTA-5A, but branched alkanes are largely excluded. A more efficient process scheme (cf. Fig. 16b), requires the “discovery” of a MOF adsorbent that would separate the di-branched isomers 22DMB and 23DMB from the nC₆, 2MP, and 3MP, these low-RON components are recycled back to the reactor. Typically, in such a processing scheme the aim would be to produce a product stream from the separation step with RON value > 92. This requirement of 92 + RON implies that the product stream will contain predominantly the di-branched isomers 22DMB and 23DMB, while allowing a small proportion of 2MP and 3MP to be incorporated into the product stream. Since high-octane gasoline is sold on the basis of the product octane value, there are no strict constraints on the product compositions and purities; i.e. sharp separations between mono- and di- branched isomers are not demanded. CBMC simulations are particularly potent tools for screening of zeolite and MOF adsorbents.
for separation of alkane isomers because the force fields for alkane molecules are well established [7,15,72,103–105].

As illustration, Fig. 17a shows the transient development of exit gas compositions from a bed packed with Co(BDP) with an equimolar 5-component feed mixture. Product gas with 92 + RON can be recovered from the displacement interval in which the di-branched isomers 22DMB and 23DMB are eluted, as indicated. When the mono-branched isomers break through, there is a sharp decrease in the RON of the product exiting the fixed bed. The desired separation is between (22DMB + 23DMB), and (nC6 + 2MP + 3MP) the appropriate expression for the separation potential is [14]

\[
\Delta Q = (Q_{nC6} + Q_{2MP} + Q_{3MP}) - \gamma_{22DMB} + \gamma_{23DMB} - (Q_{22DMB} + Q_{23DMB})
\]  

(11)

Fig. 17b compares 92 + RON productivities for ten different adsorbent materials, plotted as a function of the separation potential \(\Delta Q\); the interdependence is linear and we conclude that the best performing MOF for this separation duty is Fe2(BDP)3; this conclusion is in line with the earlier work of Herm et al. [4].

11. Separation of mixtures of xylene isomers

Aromatic hydrocarbons, that are valuable feedstocks in the petrochemical industries, are most commonly obtained from catalytic reforming of naphtha. The xylene isomers, o-xylene, m-xylene and in particular p-xylene, are important chemical intermediates. In a commonly used separation scheme (cf. Fig. 18), the xylenes rich stream from the bottom of the reformer splitter is routed to a xylenes splitter. Here, the heavier aromatics (C9+) are removed from the bottom of the column. The overhead stream from the xylenes splitter needs to be separated for recovery of p-xylene. In current technology, this mixture is separated in a Simulated Moving Bed (SMB) adsorption separation unit, that operates under conditions in which the bulk fluid phase is in the liquid state and the pores of the adsorbent are saturated with guest aromatic molecules. The typical composition of a mixed xylenes feed to the SMB adsorber packed with Co(BDP) with an equimolar 5-component feed mixture. Product gas with 92 + RON can be recovered from a bed packed with Co(BDP) also shown (right y-axis) is the RON of product gas at the outlet of fixed bed. (b) The 92 + RON productivity for ten different adsorbent materials: ZnMOF-74, MgMOF-74, Co(BDP), Fe2(BDP)3, Mn, BEA, ZIF-8, ZnHBDC, Zn(bdc)dabco, and ZIF-77, plotted as a function of the separation potential \(\Delta Q\), calculated from Eq. (9). The unary isotherm data and calculation details are provided in earlier works [13,14,37]. The computational details of the transient breakthroughs, and calculations of product RON, are provided in earlier works [13,14,37,123]; these are also summarized in the Supplementary material.

\[
\Delta Q = \frac{Q_{nC6} + Q_{2MP} + Q_{3MP}}{\gamma_{22DMB} + \gamma_{23DMB} - (Q_{22DMB} + Q_{23DMB})}
\]  

(12)

Fig. 19a presents the plot of \(\Delta Q\), versus the volumetric uptake of p-xylene for a few selected MOFs. Significant improvements over BaX zeolite are offered by DynaMOF-100 [11,109], and Co-CUK-1 [110,111]. DynaMOF-100 is a Zn(II)-based dynamic coordination framework that undergoes guest-induced structural changes so as to allow selective uptake of p-xylene within the cavities (see Fig. 19b). Co-CUK-1 is comprised of cobalt(Ii) cations and the diion of dicarboxylic acid; the 1D zig-zag shaped channels of Co-CUK-1 allow optimal vertical stacking of p-xylene (cf. Fig. 19c).

Mukherjee et al. [11] also demonstrate that DynaMOF-100 has the ability to selectively encapsulate styrene from mixtures with ethylbenzene; this separation is currently carried out in vacuum distillation columns (see top right corner of Fig. 18). The Supplementary material provides further background on styrene/ethylbenzene separations; see Figs. S92, and S93.
12. Conclusions

The following major conclusions emerge from the data and analysis presented in this article.

(1). The principles governing separations in fixed bed adsorbers and membrane permeation devices are distinctly different. The selection of the “ideal” microporous crystalline material for use in either of these devices is governed by distinctly different considerations.

(2). The membrane permeation selectivity is a product of the diffusion selectivity and the adsorption selectivity: $S_{\text{perm}} = S_{\text{diff}} \times S_{\text{ads}}$. Membrane separations are primarily “driven” by $S_{\text{diff}}$. Cage-type structures with narrow 3.3 Å to 4.3 Å windows are particularly suited for exploitation of differences in guest mobilities, as required for H₂-selective and alkene-selective permeation characteristics.

(3). Except for cage-type structures with narrow 3.3 Å to 4.3 Å windows, in all other structural topologies, adsorption strength and intra-crystalline diffusivity do not normally proceed hand-in-hand; strong adsorption almost invariably implies low mobility.

(4). Most commonly, intra-crystalline diffusional influences are undesirable in fixed bed adsorption units because these result in distended breakthroughs and reduced productivities. In case of negligible diffusional influences, the separation effectiveness for binary mixtures is dictated by a combination of adsorption selectivity, $S_{\text{ads}}$, and uptake capacities.

(5). The combined selectivity/capacity metric $\Delta Q$, derived using the idealized shock-wave model is an appropriate screening tool for selecting materials for use in PSA units. In most of the separations analyzed, the adsorbent that offers the highest value of the separation potential $\Delta Q$ is not the one that possesses the highest value of $S_{\text{ads}}$.

(6). Screening of the materials on the basis of $\Delta Q$ is particularly convenient for multicomponent separations (e.g. H₂ purification, separation of alkane isomers, and xylenes) for which there is no unambiguous definition of $S_{\text{ads}}$.

(7). For alkene/alkane separations, most of the materials developed selectively adsorb the unsaturated alkene. From a practical perspective, to meet the required 99.95%+ alkene purity target it is desirable to synthesize MOFs that selectively adsorb the saturated alkane.

Not considered in this article are separations of mixtures of polar compounds, such as water/alcohol, and alcohol/aromatic mixtures. In such cases, molecular clustering effects are of significant importance and this causes significant failure of the IAST [112,113]. There is a need for development of reliable methods for prediction of thermodynamic non-ideality effects in mixture adsorption.

Also not considered in this review are diffusion-selective separations in fixed bed adsorbers, e.g. selective uptake of N₂ from N₂/CH₄ mixtures using LTA-4A zeolite and Ba-ETS-4 [114–116], and selective uptake of O₂ from O₂/N₂ mixtures using LTA-4A zeolite and carbon molecular sieve [39,117–120]. The screening of adsorbents requires reliable experimental data on intra-crystalline diffusivities [121].
Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.seppur.2017.11.056.

References
