**Electronic Supporting Information to accompany:** 

# Tracing the Origins of Transient Overshoots for Binary Mixture Diffusion in Microporous Crystalline Materials

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### 1. Preamble

This Electronic Supporting Information (ESI) accompanying the article *Tracing the Origins of Transient Overshoots for Binary Mixture Diffusion in Microporous Crystalline Materials* provides details of (a) pure component isotherm fits, (b) modelling of mixture adsorption equilibrium, (c) calculation of thermodynamic correction factors, (d) Maxwell-Stefan diffusion equations for describing transient uptake of mixtures, and (e) methodology for simulation of transient uptake, membrane permeation, and transient breakthroughs in fixed beds.

For ease of reading, this ESI is written as a stand-alone document; as a consequence, there is some overlap of material with the main manuscript.

#### Video animations

The following set of video animations have been uploaded as ESI.

- (1) Transient development of loadings of  $CO_2/C_2H_6$  in DDR crystal at 298 K, conditions corresponding to Experiment 1 of Binder and Lauerer.  $CO_2$  exhibits spatio-temporal overshoots.
- (2) Transient development of loadings of  $CO_2/C_2H_6$  in DDR crystal at 298 K, conditions corresponding to Experiment 2 of Binder and Lauerer.  $CO_2$  exhibits spatio-temporal overshoots.
- (3) Transient development of loadings of  $CO_2/C_2H_6$  in DDR crystal at 298 K, conditions corresponding to Experiment 3 of Binder and Lauerer.  $CO_2$  exhibits spatio-temporal overshoots.
- (4) Transient development of loadings of N<sub>2</sub>/CH<sub>4</sub> uptake in LTA-4A at 194 K: simulation of Habgood experiment. N<sub>2</sub> exhibits spatio-temporal overshoots.
- (5) Transient development of loadings of O<sub>2</sub>/N<sub>2</sub> in CMS at 300 K, simulation of Chen experiment. O<sub>2</sub> exhibits spatio-temporal overshoots.
- (6) Transient development of loadings of nC6/2MP in MFI at 298 K, simulation of Run 1 of Titze. nC6 exhibits spatio-temporal overshoots.
- (7) Transient development of loadings of ethane/n-pentane mixture in extrudates of activated carbon at 303 K. Ethane exhibits spatio-temporal overshoots.

- (8) Transient development of loadings of  $C_3H_6/C_3H_8$  in ZIF-8 at 298 K taking  $D_1/D_2 = 125$ .  $C_3H_6$  exhibits spatio-temporal overshoots.
- (9) Transient development of loadings of 2MB/2MP/22DMB in MFI extrudate. Note that both 2MB and 2MP exhibit spatio-temporal overshoots
- (10) Transient breakthrough of 2MB/2MP/22DMB mixture in fixed bed of MFI extrudates; these are the simulations of Run 20 of Jolimaître et al.
- (11) Transient development of ethanol/1-propanol loadings in CHA zeolite. Ethanol exhibits spatiotemporal overshoots.
- (12) Transient development of CH<sub>4</sub>/nC<sub>4</sub>H<sub>10</sub> loadings in MFI membrane. CH<sub>4</sub> exhibits spatio-temporal overshoots.
- (13) Transient development of  $H_2/nC_4H_{10}$  loadings in MFI membrane.  $H_2$  exhibits spatio-temporal overshoots.
- (14) Transient development of nC6/2MP loadings in MFI membrane. nC6 exhibits spatio-temporal overshoots.
- (15) Transient development of water/ethanol loadings in DDR pervaporation membrane. Water exhibits spatio-temporal overshoots.
- (16) Transient development of water/ethanol loadings in LTA-4A pervaporation membrane. Water exhibits spatio-temporal overshoots.
- (17) Transient development of loadings of 2MP/22DMB in MFI catalyst carrying out the isomerization reaction 2MP(1) 
  ≥ 22DMB(2). 2MP exhibits spatio-temporal overshoots.
- (18) Transient development of loadings of nC6/3MP/22DMB in MFI catalyst carrying out the isomerization reaction nC6(1) 
  → 3MP(2) → 22DMB(3). nC6 exhibits spatio-temporal overshoots.

- (19) Transient development of loadings of m-xylene/p-xylene in MFI catalyst carrying out the isomerization reaction m-xylene(1) ⇒ p-xylene(2). p-xylene exhibits spatio-temporal overshoots.
- (20) Transient development of loadings of ethene/benzene/ethylbenzene in MFI catalyst carrying out the reaction ethene(1)+benzene(2) the ethylbenzene(3). Ethene exhibits spatio-temporal

overshoots.

These animations provide some "feel" of spatio-temporal overshoots of during transient uptake, membrane permeation, and transient breakthroughs in fixed-bed adsorbers.

## 2. The Babbitt equation for unary diffusion in micropores

Within microporous crystalline materials, the guest molecules exist in the adsorbed phase. The Gibbs adsorption equation<sup>1</sup> in differential form is

$$Ad\pi = \sum q_i d\mu_i \tag{1}$$

The quantity A on the left side of Equation (1) is the surface area per kg of framework, with units of  $m^2$  per kg of the framework of the crystalline material;  $q_i$  is the molar loading of component *i* in the adsorbed phase with units moles per kg of framework;  $\mu_i$  is the molar chemical potential of component *i*. The spreading pressure  $\pi$  has the same units as surface tension, i.e. N m<sup>-1</sup>; indeed the spreading pressure is the negative of the surface tension.<sup>2</sup>

For describing the *unary* transport of bound moisture in wood, Babbitt<sup>3, 4</sup> suggested the use of the gradient of the spreading pressure  $\partial \pi / \partial r$  as the thermodynamically correct driving force. The units of  $\partial \pi / \partial r$  are N m<sup>-2</sup>, and this represents the force acting per m<sup>2</sup> of material surface. The number of moles of adsorbate per m<sup>2</sup> of surface is  $\frac{q_i}{A}$ . Therefore the force per mole of adsorbate is

 $-\left(\frac{\partial \pi}{\partial r}\right) / \left(\frac{q_i}{A}\right) = -\frac{\partial \mu_i}{\partial r}$ . This force is balanced by friction between the mobile adsorbates and the

surface of the material.

$$-\left(\frac{\partial \pi}{\partial r}\right) / \left(\frac{q_i}{A}\right) = \frac{RT}{D_i} u_i; \quad -\frac{\partial \mu_i}{\partial r} = \frac{RT}{D_i} u_i$$
(2)

where  $u_i$  is the velocity of motion of the adsorbate with respect to the framework material. The quantity  $\frac{RT}{D_i}$  in the right member of equation (2) is interpreted as the "drag coefficient". The unary diffusivity  $D_i$ , with the units m<sup>2</sup> s<sup>-1</sup>, is to be interpreted as an inverse drag coefficient between the adsorbate and the surface. If we define  $N_i$  as the number of moles of species *i* transported per m<sup>2</sup> of crystalline material per second

$$N_i = \rho q_i u_i \tag{3}$$

where  $\rho$  is the framework density with units of kg m<sup>-3</sup>, we obtain the flux relation

$$-\rho \frac{A}{RT} \frac{\partial \pi}{\partial r} = \frac{N_i}{D_i}$$
(4)

Combining Equation (1) and (4) we obtain

$$-\rho \frac{q_i}{RT} \frac{\partial \mu_i}{\partial r} = \frac{N_i}{D_i}$$
(5)

Equation (5) is the familiar form of the Maxwell-Stefan (M-S) formulation<sup>5-7</sup> for unary diffusion.

The chemical potential gradient can be related to the gradient of the molar loading by defining a thermodynamic correction factor  $\Gamma_i$ 

$$\frac{q_i}{RT}\frac{\partial\mu_i}{\partial r} = \Gamma_i \frac{\partial q_i}{\partial r}; \quad \Gamma_i \equiv \frac{q_i}{p_i}\frac{\partial p_i}{\partial q_i}$$
(6)

Combining Equations (5) and (6) we may write

$$N_{i} = -\rho D_{i} \frac{q_{i}}{RT} \frac{\partial \mu_{i}}{\partial r} = -\rho D_{i} \Gamma_{i} \frac{\partial q_{i}}{\partial r}$$

$$\tag{7}$$

The product of the M-S diffusivity and the thermodynamic correction factor is the Fick diffusivity

$$D_i = \mathcal{D}_i \Gamma_i \tag{8}$$

The magnitude of the M-S diffusivity varies with the spreading pressure. The spreading pressure can be determined from knowledge of the unary adsorption isotherm, q(p), fitted with say the dual-Langmuir-Freundlich isotherm

$$q(p) = q_{A,sat} \frac{b_A p^{\nu_A}}{1 + b_A p^{\nu_A}} + q_{B,sat} \frac{b_B p^{\nu_B}}{1 + b_B p^{\nu_B}}$$
(9)

The spreading pressure is given by

$$\frac{\pi A}{RT} = \int_{0}^{p} \frac{q(p)}{p} dp \tag{10}$$

The units of  $\frac{\pi A}{RT}$ , also called the adsorption potential,<sup>8</sup> are mol kg<sup>-1</sup>.

For the 2-site Langmuir-Freundlich isotherm, the integration yields

$$\frac{\pi A}{RT} = \int_{P=0}^{P} \frac{q(p)}{p} dp = \frac{q_{A,sat}}{v_A} \ln\left(1 + b_A P^{v_A}\right) + \frac{q_{B,sat}}{v_B} \ln\left(1 + b_B P^{v_B}\right)$$
(11)

Figures 1a, b, c presents MD data on the M-S diffusivities of various guest molecules in (a) all-silica FAU zeolite, (b) MFI zeolite, and (c) IRMOF-1. The MD data are at 300 K. The x-axis is the  $\frac{\pi A}{RT}$  calculated on the basis of the molar loadings used in the MD simulations, in conjunction with CBMC simulation data for the unary isotherms of the guest molecules. The dependence of the M-S diffusivities on  $\frac{\pi A}{RT}$  varies with different host materials. This aspect is best illustrated by the Figure 1d that compares the M-S diffusivity of CH<sub>4</sub> in various host materials.

Preferential location of molecules within the structural framework can cause strong isotherm inflections. For example, branched alkanes, benzene, alkyl benzenes, and cyclohexane prefer to locate at the channel intersections of MFI zeolite due to extra "leg-room" and other configurational considerations.<sup>9</sup> There are only 4 intersection sites available per unit cell of MFI. This implies that to obtain loadings higher than  $\Theta_i = 4$  molecules per unit cell, an extra "push" will be required to locate the molecules elsewhere within the channels; this leads to isotherm inflection. Due to strong isotherm inflections, the  $1/\Gamma_i$  exhibits a cusp-like inflection at a loading of  $\Theta_i = 4$ , when all the preferred adsorption sites are occupied; is demonstrated in the data on  $1/\Gamma_i$  for iso-butane/MFI in Figures 2. In the range  $0 < \Theta_i < 4$ ,  $1/\Gamma_i$  decreases nearly linearly with  $\Theta_i$  signifying the fact that the vacancy *decreases* almost linearly with loading. For  $\Theta_i > 4$ ,  $1/\Gamma_i$  increases with  $\Theta_i$  because additional sites *within* the MFI channels are created to accommodate more than 4 molecules per unit cell, i.e. the number of available sites *increases* within this loading range. These additional sites must be accommodated within the channels, requiring the additional "push" that caused the inflection.

When molecular clustering occurs  $1/\Gamma_i$  can exceed unity; such clustering may occur when the operating temperature is below the critical temperature of the guest molecule.<sup>10</sup> Figure 3 presents the experimental data of Chmelik et al.<sup>11</sup>, for the loading dependence of n-butane (nC4,  $T_c = 425$  K), isobutane (iC4,  $T_c = 408$  K), neopentane (neo-P,  $T_c = 434$  K), and 2-methylbutane (2MB,  $T_c = 460$  K) at T = 298 K, significantly lower than the critical temperatures of each of the four guest species. For all four guest molecules the dependence of M-S diffusivities on the spreading pressure goes hand-in-hand with the corresponding dependence of  $1/\Gamma_i$ .

### 3. The Maxwell-Stefan relations for *n*-component diffusion in micropores

The best starting point for developing the Maxwell-Stefan formulation for mixture diffusion is Equation (2), that needs extension. The force acting per mole of adsorbate species i is balanced by (1)

friction between i and the pore walls (this is the same term as for unary transport), and (2) friction between species i and species j. We may write

$$-\frac{1}{RT}\frac{\partial\mu_i}{\partial r} = \sum_{j=1\atop j\neq i}^n \frac{x_j}{D_{ij}} \left(u_i - u_j\right) + \frac{1}{D_i} \left(u_i\right); \quad i = 1, 2..n$$
(12)

The  $x_i$  in equations (12) represent the component mole fractions in the adsorbed phase within the pores

$$x_i = q_i / q_i; \quad q_i = \sum_{i=1}^n q_i; \quad i = 1, 2, ..n$$
 (13)

The  $D_i$  have the same significance as for unary diffusion; they are inverse drag coefficients between the species *i* and the material surface. Indeed, an important persuasive advantage of the M-S equations is that the  $D_i$  for mixture diffusion often retains the same magnitude and loading dependence as for unary diffusion.<sup>5, 12, 13</sup>

The  $D_{ij}$  may be interpreted as the inverse drag coefficient between species *i* and species *j*. At the molecular level, the  $D_{ij}$  reflect how the facility for transport of species *i correlates* with that of species *j*; they are also termed *exchange coefficients*. The multiplication factor  $x_j$  has been introduced in the numerator of the first right member of equation (12) because the friction experience by species *i* with the each of the other species in the adsorbed phase (j = 2, 3, ..n) should be proportional to the relative amounts of species *j* (= 2, 3, ..*n*) in the adsorbed phase. Expressing the velocities  $u_j$  in terms of the intra-crystalline diffusion fluxes  $u_i = N_i / \rho q_i$ 

$$-\frac{\rho}{RT}\frac{\partial\mu_i}{\partial r} = \sum_{j=1\atop j\neq i}^n \frac{X_j}{D_{ij}} \left(\frac{N_i}{q_i} - \frac{N_j}{q_j}\right) + \frac{1}{D_i} \left(\frac{N_i}{q_i}\right); \quad i = 1, 2...n$$
(14)

Multiplying both sides of equation (14) by  $x_i$  we get

$$-\rho \frac{x_i}{RT} \frac{\partial \mu_i}{\partial r} = \sum_{j=1\atop j\neq i}^n \frac{x_i x_j}{D_{ij}} \left( \frac{N_i}{q_i} - \frac{N_j}{q_j} \right) + \frac{1}{D_i} \left( \frac{x_i N_i}{q_i} \right); \quad i = 1, 2...n$$
(15)

In view of the equation (13), we may simplify equation (15) to write

$$-\rho \frac{q_i}{RT} \frac{\partial \mu_i}{\partial r} = \sum_{j=1\atop j\neq i}^n \left( \frac{x_j N_i - x_i N_j}{D_{ij}} \right) + \frac{N_i}{D_i}; \quad i = 1, 2...n$$
(16)

The Onsager reciprocal relations demand the symmetry constraint

$$D_{ij} = D_{ji}; \quad i, j = 1, 2, \dots n$$
(17)

As discussed in the following section, the exchange coefficients  $D_{ij}$  bear a relation with the M-S diffusivity in the fluid mixture,  $D_{ij,fl}$ ; this is an important advantage of the M-S formulation.

An entirely analogous manner of writing equation (16) is in terms of molar concentrations  $c_i$ , in the adsorbed phase, based on the accessible pore volume,  $V_p$  ( = m<sup>3</sup> pore volume per kg framework)

$$c_i = \frac{q_i}{V_p}; \quad c_t = \sum_{i=1}^n c_i = \frac{q_t}{V_p}$$
 (18)

This alternative formulation:

$$-\rho V_p \frac{c_i}{RT} \frac{\partial \mu_i}{\partial r} = \sum_{j=1\atop j\neq i}^n \left( \frac{x_j N_i - x_i N_j}{D_{ij}} \right) + \frac{N_i}{D_i}; \quad i = 1, 2...n$$
(19)

The quantity  $\rho V_p$  is the fractional pore volume

$$\rho V_p = \left(\frac{\text{kg framework}}{\text{m}^3 \text{ framework}}\right) \left(\frac{\text{m}^3 \text{ pore volume}}{\text{kg framework}}\right) = \left(\frac{\text{m}^3 \text{ pore volume}}{\text{m}^3 \text{ framework}}\right) = \varepsilon$$
(20)

So, we re-write equation (19) in the form

$$-\varepsilon \frac{c_i}{RT} \frac{\partial \mu_i}{\partial r} = \sum_{j=1\atop j\neq i}^n \left( \frac{x_j N_i - x_i N_j}{D_{ij}} \right) + \frac{N_i}{D_i}; \quad i = 1, 2...n$$
(21)

The formulation (21) has been employed to develop a unified theory of mixture diffusion in both micropores and mesopores.<sup>12, 14-16</sup> The fluxes  $N_i$  in equation (21), and in this entire article are defined in terms of the moles transported per m<sup>2</sup> of the *total surface of crystal material*. Alternatively, if we just

focus on fluxes inside a single pore, it is convenient to define the fluxes  $N_i$  in terms of the moles transported per m<sup>2</sup> surface of the pore, then the factor  $\rho V_p$  has to be omitted in the left member of equation (21).

Early publications<sup>17-20</sup> on *n*-component mixture diffusion in micropores have been developed the M-S formulation in a different manner, using the fractional occupancies,  $\theta_i$ , of species *i* in relation to the saturation capacities,  $q_{i,sat}$ , for adsorption of each species

$$\theta_i = \frac{q_i}{q_{i,sat}}; \quad i = 1, 2, \dots$$
(22)

as multiplication factor on the right member of equation (12). In this case we write

$$-\frac{1}{RT}\frac{\partial\mu_i}{\partial r} = \sum_{\substack{j=1\\j\neq i}}^n \frac{\theta_j}{D_{ij}^{\theta}} (u_i - u_j) + \frac{1}{D_i} (u_i); \quad i = 1, 2..n$$
(23)

The superscript  $\theta$  on the exchange coefficients  $D_{ij}^{\theta}$  serves as a reminder that these coefficients are distinct from those defined in equation (12).

Expressing the velocities  $u_j$  in terms of the intra-crystalline diffusion fluxes  $u_i = N_i / \rho q_i$  we get

$$-\frac{1}{RT}\frac{\partial\mu_i}{\partial r} = \sum_{\substack{j=1\\j\neq i}}^n \frac{\theta_j}{D_{ij}^{\theta}} \left(\frac{N_i}{\rho q_i} - \frac{N_j}{\rho q_j}\right) + \frac{1}{D_i} \left(\frac{N_i}{\rho q_i}\right); \quad i = 1, 2..n$$
(24)

Multiplying both sides of equation (24) by  $\theta_i$  and re-arranging we get

$$-\rho \frac{\theta_i}{RT} \frac{\partial \mu_i}{\partial r} = \sum_{j=1\atop j\neq i}^n \frac{\theta_i \theta_j}{\theta_{ij}} \left( \frac{N_i}{q_i} - \frac{N_j}{q_j} \right) + \frac{\theta_i}{\theta_i} \left( \frac{N_i}{q_i} \right); \quad i = 1, 2..n$$
(25)

In view of equation (22), equation (25) can be re-arranged to

$$-\rho \frac{\theta_i}{RT} \frac{\partial \mu_i}{\partial r} = \sum_{j=1\atop j \neq i}^n \left( \frac{q_j N_i - q_i N_j}{q_{i,sat} q_{j,sat} \mathcal{D}_{ij}^{\theta}} \right) + \frac{N_i}{q_{i,sat} \mathcal{D}_i}; \quad i = 1, 2..n$$
(26)

The Onsager reciprocal relations demand the symmetry

$$q_{j,sat}D_{ij}^{\theta} = q_{i,sat}D_{ji}^{\theta}; \quad i = 1, 2..n$$
 (27)

The two sets of exchange coefficients defined in equations (12) and (23) are inter-related

$$q_{j,sat} \mathcal{D}_{ij}^{\theta} / q_t = \mathcal{D}_{ij} = \mathcal{D}_{ji} = c_{i,sat} \mathcal{D}_{ji}^{\theta} / q_t$$
(28)

The exchange coefficients  $D_{ij}^{\theta}$  cannot be simply related to the fluid phase M-S diffusivity,  $D_{12,fl}$ . It is for this reason that we prefer the formulation in equation (16).

If the saturation capacities of all of the individual species are (nearly) equal to one another, equation (26) can be simplified to yield

$$-\rho \frac{1_i}{RT} \frac{\partial \mu_i}{\partial r} = \sum_{\substack{j=1\\j\neq i}}^n \left( \frac{\theta_j N_i - \theta_i N_j}{D_{ij}^{\theta}} \right) + \frac{N_i}{D_i}; \quad i = 1, 2..n$$
(29)

The important advantage of the use of equation (29) is that by combining with the mixed-gas Langmuir model for mixture adsorption (discussed below), analytical solutions can be derived for the membrane permeation fluxes, and effectiveness factors.<sup>21-24</sup>

In this article, we use the M-S formulation given by equations (16).

# 4. The Maxwell-Stefan relations for binary mixture diffusion in micropores

For binary mixture diffusion inside porous crystalline materials the Maxwell-Stefan equations (16) are written as

$$-\rho \frac{q_1}{RT} \frac{\partial \mu_1}{\partial r} = \frac{x_2 N_1 - x_1 N_2}{D_{12}} + \frac{N_1}{D_1} -\rho \frac{q_2}{RT} \frac{\partial \mu_2}{\partial r} = \frac{x_1 N_2 - x_2 N_1}{D_{12}} + \frac{N_2}{D_2}$$
(30)

The first members on the right hand side of Equation (30) are required to quantify slowing-down effects that characterize binary mixture diffusion.<sup>5, 12, 25</sup> There is no experimental technique for direct determination of the exchange coefficients  $D_{12}$ , that quantify molecule-molecule interactions. Molecular dynamics (MD) simulation data from the literature<sup>5, 12, 13, 20, 26, 27</sup> provide the further insights into the ESI 13

characteristics of the exchange coefficients  $D_{12}$ . Figure 4 presents MD data for  $D_{12}$  for six equimolar binary mixtures equimolar ( $q_1 = q_2$ ) binary mixtures (a) H<sub>2</sub>/CH<sub>4</sub>, (b) CH<sub>4</sub>/Ar, (c) CH<sub>4</sub>/C<sub>2</sub>H<sub>6</sub>, (d) CO<sub>2</sub>/CH<sub>4</sub>, (e) CO<sub>2</sub>/H<sub>2</sub>, and (f) CO<sub>2</sub>/N<sub>2</sub> at 300 K, in a variety of micro-porous host materials with varying pore size, pore topology and pore connectivity. Also included are MD data for mesoporous BTP-COF with hexagonal channels of 3.4 nm size. The data are compared at the total mixture pore concentration,  $c_i = (q_1 + q_2)/V_p$ .

For mesoporous materials with pores in the 20 Å to 100 Å size range the values of the exchange coefficient  $D_{12}$  are the nearly the same as the binary *fluid phase* M-S diffusivity,  $D_{12,fl}$ , over the entire range of pore concentrations.<sup>5, 12, 15, 27</sup> For micro-porous materials, the exchange coefficient  $D_{12}$  cannot be directly identified with the corresponding fluid phase diffusivity  $D_{12,fl}$  because the molecule-molecule interactions are also significantly influenced by molecule-wall interactions. For microporous materials, the exchange coefficients  $D_{12}$  are lower than the corresponding values of  $D_{12,fl}$  by a factor that depends on the pore size, connectivity and topology.<sup>5, 12, 15, 27</sup> Procedures for estimation of the  $D_{12,fl}$  are available in Poling et al.,<sup>28</sup> and therefore this provides a convenient starting point for the estimation of the  $D_{12}$ .

For purposes of calculations of the uptake within crystals and permeation fluxes across membranes, we need to calculate the chemical potential gradients,  $\frac{\partial \mu_i}{\partial r}$ , where *r* is the radius of a spherical crystal or distance along the membrane thickness. For an ideal gas mixture, the chemical potential gradients can be related to the partial pressure gradients in the bulk gas phase mixture

$$\frac{\partial \mu_i}{\partial r} = RT \frac{\partial \ln p_i}{\partial r} = RT \frac{1}{p_i} \frac{\partial p_i}{\partial r}$$
(31)

The gradients in the chemical potential can be related to the gradients of the molar loadings by defining thermodynamic correction factors  $\Gamma_{ij}$ 

$$\frac{q_i}{RT}\frac{\partial\mu_i}{\partial r} = \sum_{j=1}^2 \Gamma_{ij}\frac{\partial q_j}{\partial r}; \quad \Gamma_{ij} = \frac{q_i}{p_i}\frac{\partial p_i}{\partial q_j}; \quad i, j = 1,2$$
(32)

#### In 2-dimensional matrix notation, equation (32) takes the form

$$-\left(\frac{q_1}{RT}\frac{\partial\mu_1}{\partial r}\right)_{\frac{q_2}{RT}\frac{\partial\mu_2}{\partial r}} = \left[\Gamma\right] \left(\frac{\frac{\partial q_1}{\partial r}}{\frac{\partial q_2}{\partial r}}\right)$$
(33)

The thermodynamic correction factors  $\Gamma_{ij}$  can be calculated by differentiation of the model describing mixture adsorption equilibrium. Generally speaking, the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz<sup>2</sup> is the preferred method for estimation of mixture adsorption equilibrium. In some special case, the mixed-gas Langmuir model

$$\frac{q_1}{q_{1,sat}} = \theta_1 = \frac{b_1 p_1}{1 + b_1 p_1 + b_2 p_2}; \quad \frac{q_2}{q_{2,sat}} = \theta_2 = \frac{b_2 p_2}{1 + b_1 p_1 + b_2 p_2}$$
(34)

may be of adequate accuracy.

For the mixed-gas Langmuir model, equation (34), we can derive simple analytic expressions for the four elements of the matrix of thermodynamic factors:<sup>17</sup>

$$\begin{bmatrix} \Gamma_{11} & \Gamma_{12} \\ \Gamma_{21} & \Gamma_{22} \end{bmatrix} = \frac{1}{1 - \theta_1 - \theta_2} \begin{bmatrix} 1 - \theta_2 & \frac{q_{1,sat}}{q_{2,sat}} \theta_1 \\ \frac{q_{2,sat}}{q_{1,sat}} \theta_2 & 1 - \theta_1 \end{bmatrix}$$
(35)

where the fractional occupancies,  $\theta_i$ , are defined by Equation (22).

The elements of the matrix of thermodynamic factors  $\Gamma_{ij}$  can be calculated explicitly from information on the component loadings  $q_i$  in the adsorbed phase; this is the persuasive advantage of the use of the mixed-gas Langmuir model. By contrast, the IAST does not allow the calculation of  $\Gamma_{ij}$  explicitly from knowledge on the component loadings  $q_i$  in the adsorbed phase; an iterative procedure is required.

Let us define the square matrix [B]

$$[B] = \begin{bmatrix} \frac{1}{D_1} + \frac{x_2}{D_{12}} & -\frac{x_1}{D_{12}} \\ -\frac{x_2}{D_{12}} & \frac{1}{D_2} + \frac{x_1}{D_{12}} \end{bmatrix}$$
(36)

Equation (30) can be re-cast into 2-dimensional matrix notation

$$-\rho \left( \frac{\frac{q_1}{RT} \frac{\partial \mu_1}{\partial r}}{\frac{q_2}{RT} \frac{\partial \mu_2}{\partial r}} \right) = \left[ B \right] \binom{N_1}{N_2}; \quad \binom{N_1}{N_2} = -\rho \left[ B \right]^{-1} \left( \frac{\frac{q_1}{RT} \frac{\partial \mu_1}{\partial r}}{\frac{q_2}{RT} \frac{\partial \mu_2}{\partial r}} \right)$$
(37)

The inverse of the square matrix [B] can be obtained explicitly

$$[B]^{-1} = \frac{1}{1 + \frac{x_1 D_2}{D_{12}} + \frac{x_2 D_1}{D_{12}}} \begin{bmatrix} D_1 \left( 1 + \frac{x_1 D_2}{D_{12}} \right) & \frac{x_1 D_1 D_2}{D_{12}} \\ \frac{x_2 D_1 D_2}{D_{12}} & D_2 \left( 1 + \frac{x_2 D_1}{D_{12}} \right) \end{bmatrix}$$
(38)

Combining equations (33), (37), and (38) we obtain

$$\binom{N_{1}}{N_{2}} = -\frac{\rho}{1 + \frac{x_{1}D_{2}}{D_{12}} + \frac{x_{2}D_{1}}{D_{12}}} \begin{bmatrix} D_{1}\left(1 + \frac{x_{1}D_{2}}{D_{12}}\right) & \frac{x_{1}D_{1}D_{2}}{D_{12}} \\ \frac{x_{2}D_{1}D_{2}}{D_{12}} & D_{2}\left(1 + \frac{x_{2}D_{1}}{D_{12}}\right) \end{bmatrix} \begin{bmatrix} \Gamma_{11} & \Gamma_{12} \\ \Gamma_{21} & \Gamma_{22} \end{bmatrix} \begin{pmatrix} \frac{\partial q_{1}}{\partial r} \\ \frac{\partial q_{2}}{\partial r} \\ \frac{\partial q_{2}}{\partial r} \end{pmatrix}$$
(39)

The ratio  $(D_1/D_{12})$  is a reflection of the *degree of correlations*. We consider correlation effects to be strong when  $D_1/D_{12} > 1$ . Figure 5 shows MD data on  $D_1/D_{12}$  for diffusion of six different mixtures (a) H<sub>2</sub>/CO<sub>2</sub>, (b) CO<sub>2</sub>/CH<sub>4</sub>, (c) H<sub>2</sub>/CH<sub>4</sub>, (d) CH<sub>4</sub>/nC<sub>4</sub>H<sub>10</sub>, (e) CH<sub>4</sub>/C<sub>2</sub>H<sub>6</sub>, and (f) CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub> in a variety of host materials, expressed as a function of the total concentration,  $c_t$ , of the adsorbed mixture within the pores. The use of pore concentrations  $c_t$  rather than the molar loadings affords a fairer comparison of different host materials as explained in previous works.<sup>15</sup> For any guest/host combination,  $D_1/D_{12}$  is seen to increase as the pore concentration increases; this implies that correlation effects are expected to be stronger for separations operating at higher pressures.

Consider Figure 5c that compares the data on  $D_1/D_{12}$  for H<sub>2</sub>(1)/CH<sub>4</sub>(2) mixtures in several hosts. For H<sub>2</sub>(1)/CH<sub>4</sub>(2) mixtures, correlations are strongest in mesoporous BTP-COF, one-dimensional (1D) channel structures (e.g. MgMOF-74), intersecting channels (e.g. MFI), and "open" structures (e.g. NaX zeolite, CuBTC, IRMOF-1) consisting of large cages separated by wide windows. Strong correlation

effects cause slowing-down of more-mobile-less-strongly-adsorbed molecules by tardier-more-stronglyadsorbed-partner species. For example, the mobility of less-strongly-adsorbed H<sub>2</sub> in the intersecting channels of MFI zeolite, is significantly retarded by the presence of its more-strongly-adsorbed-partner CH<sub>4</sub>.

Extensive Molecular Dynamics (MD) simulations have shown that correlation effects are of negligible importance for mixture diffusion across materials such as LTA, ZIF-8, CHA, DDR, ERI that consist of cages separated by windows in the 3.4 Å – 4.2 Å size range.<sup>5, 12, 25, 29</sup> Molecules jump one-ata-time across the narrow windows, and the assumption of negligible correlations is justified. As verification, we note from Figure 5c, that  $D_1/D_{12} < 1$  for H<sub>2</sub>(1)/CH<sub>4</sub>(2) mixture diffusion in LTA zeolite.

In cases in which correlations are negligible, Equation (39) simplifies to yield

$$\begin{pmatrix} N_1 \\ N_2 \end{pmatrix} = -\rho \begin{bmatrix} D_1 & 0 \\ 0 & D_2 \end{bmatrix} \begin{bmatrix} \Gamma_{11} & \Gamma_{12} \\ \Gamma_{21} & \Gamma_{22} \end{bmatrix} \begin{pmatrix} \frac{\partial q_1}{\partial r} \\ \frac{\partial q_2}{\partial r} \\ \frac{\partial q_2}{\partial r} \end{pmatrix} = -\rho \begin{bmatrix} D_1 & 0 \\ 0 & D_2 \end{bmatrix} \begin{pmatrix} \frac{\partial (\Gamma_{11}q_1 + \Gamma_{12}q_2)}{\partial r} \\ \frac{\partial (\Gamma_{21}q_1 + \Gamma_{22}q_2)}{\partial r} \end{pmatrix}$$
(40)

From Equation (40) we note that the intra-crystalline fluxes  $N_1$ , and  $N_2$  are, respectively, proportional to the gradients of the corrected loadings  $q_1(\mu_1 - \mu_1^0)/RT = \Gamma_{11}q_1 + \Gamma_{12}q_2$ , and  $q_2(\mu_2 - \mu_2^0)/RT = \Gamma_{21}q_1 + \Gamma_{22}q_2$ . Here,  $\mu_i^0$  is the chemical potential of species *i* at the standard state.

# 5. Simulation methodology for transient uptake in microporous particle

For most crystal geometries, representation as an equivalent sphere is an acceptable approximation.<sup>1</sup> Indeed, most researchers report their uptake diffusivities in terms of a model that assumes uptake within a single spherical crystalline particle. The values thus obtained for the diffusivities within a spherical crystal can be translated to other crystal geometries by comparing values at the same characteristic dimension, defined as the ratio of the crystal volume to its external suface area. For a spherical shaped

crystal of radius  $r_c$ , the ratio of the volume to the external surface area is

a is 
$$\frac{\left(\frac{4}{3}\pi r_c^3\right)}{4\pi r_c^2} = \frac{r_c}{3}$$

The radial distribution of molar loadings,  $q_i$ , within a spherical crystallite, of radius  $r_c$ , is obtained from a solution of a set of differential equations describing the uptake

$$\rho \frac{\partial q_i(r,t)}{\partial t} = -\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 N_i \right) \tag{41}$$

The fluxes  $N_i$ , in turn, are related to the radial gradients in the molar loadings by Equation (39), or the simplified Equation (40). At time t = 0, i.e. the initial conditions, the molar loadings  $q_i(r,0)$  at all locations r within the crystal are uniform (zero loadings). For all times  $t \ge 0$ , the exterior of the crystal is brought into contact with a bulk gas mixture at partial pressures  $p_i(r_c,t)$  that is maintained constant till the crystal reaches thermodynamic equilibrium with the surrounding gas mixture.

$$t \ge 0; \quad q_i(r_c, t) \text{ in equilibrium with the initial values } p_i(r_c, t)$$

$$(42)$$

At any time t, during the transient approach to thermodynamic equilibrium, the spatial-averaged component loading within the crystallites of radius  $r_c$  is calculated using

$$\bar{q}_{i}(t) = \frac{3}{r_{c}^{3}} \int_{0}^{r_{c}} q_{i}(r,t) r^{2} dr$$
(43)

The spatial-averaged  $\overline{q}_i(t)$  can be compared directly with experimental transient uptake data.

In the concentration measures of adsorbed phase is terms of the molar concentrations  $c_i = \frac{q_i}{V_p}$ , the

equation (41) is equivalent to

$$\rho V_p \frac{\partial c_i(r,t)}{\partial t} = \varepsilon \frac{\partial c_i(r,t)}{\partial t} = -\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 N_i \right)$$
(44)

There is no generally applicable analytical solution to describe transient diffusion of binary mixtures and the set of Equations (39), (41), (42), and (43) need to be solved numerically using robust computational techniques. Equations (41) are first subjected to finite volume discretization. One of two strategies can be adopted: (a) equi-volume discretization, or (b) equi-distant discretization; see Figure 6. The choice of the discretization scheme used is crucially important in obtaining accurate, converged results. The choice of equi-volume slices is needed when the gradients of the loadings are particularly steep nearer to  $r = r_c$ . For either strategy, about 100 – 400 slices are employed, depending on the guest/host combination. Combination of the discretized partial differential equations (41) along with algebraic equations describing mixture adsorption equilibrium, results in a set of differential-algebraic equations (DAEs), which are solved using BESIRK.<sup>30</sup> BESIRK is a sparse matrix solver, based on the semi-implicit Runge-Kutta method originally developed by Michelsen,<sup>31</sup> and extended with the Bulirsch-Stoer extrapolation method.<sup>32</sup> Use of BESIRK improves the numerical solution efficiency in solving the set of DAEs. The evaluation of the sparse Jacobian required in the numerical algorithm is largely based on analytic expressions.<sup>17</sup> Further details of the numerical procedures used in this work, are provided by Krishna and co-workers;<sup>17, 26, 33, 34</sup> interested readers are referred to our website that contains the numerical details.<sup>33</sup>

### 6. Simulation methodology for transient membrane permeation

Thin microporous layers of zeolites, MOFs, and ZIFs have potential applications in membrane separations. The transient permeation fluxes  $N_i$ , defined in terms of the cross-sectional area of the membrane, are obtained by solving the set of partial differential equations

$$\frac{\partial q_i(z,t)}{\partial t} = -\frac{1}{\rho} \frac{\partial}{\partial z} (N_i)$$
(45)

where z is the distance coordinate along the direction of membrane thickness. In the general case when correlations are of importance, we need to use the M-S Equation (39) to describe the permeation fluxes.

For host materials such as DDR, CHA, ZIF-8, LTA-4A, correlations are of negligible importance because the guest molecules jump one-at-a-time across the narrow windows; in these circumstances, the simplified Equation (40) are used to describe permeation fluxes.

The boundary conditions are the partial pressures and component molar loadings at the upstream (z = 0) and downstream ( $z = \delta$ ) faces of the membrane; see schematic in Figure 7.

$$z = 0; \quad p_i = p_{i0}; \quad q_i = q_{i0}$$
  

$$z = \delta; \quad p_i = p_{i\delta}; \quad q_i = q_{i\delta}$$
(46)

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The membrane permeation selectivity,  $S_{perm}$ , is usually defined by

$$S_{perm} = \frac{N_1 / (p_{10} - p_{1\delta})}{N_2 / (p_{20} - p_{2\delta})}$$
(47)

The solution of Equation (39), and (45) requires discretization of the membrane layer into slices, about 100-200 in number, and solving the resulting set of differential-algebraic equations (DAE) using the same numerical procedures as for transient uptake within crystals.

A major proportion of the membrane permeation data available in the literature pertains to MFI zeolite membranes. Figure 8 presents a summary of the MD simulation data for the degree of correlations,  $D_1/D_{12}$ , for diffusion of equimolar binary H<sub>2</sub>(1)/CH<sub>4</sub>(2), CH<sub>4</sub>(1)/nC<sub>4</sub>H<sub>10</sub>(2), CH<sub>4</sub>(1)/CO<sub>2</sub>(2), and H<sub>2</sub>(1)/CO<sub>2</sub>(2) mixtures in MFI zeolite at 300 K, as a function of the total mixture loading,  $q_t$ . Typically, the mixture molar loadings in the membrane layer will be in the range of 1 – 4 mol kg<sup>-1</sup>. From the data in Figure 8 we must conclude that correlation effects will have an important bearing on the mixture permeation characteristics.

To provide a feel for the magnitude of slowing-down effects in membrane permeation we investigated the influence of  $D_1/D_{12}$  on the steady-state permeation selectivity,  $S_{perm}$  (defined in Equation (47)), of binary 95/5 CH<sub>4</sub>(1)/nC<sub>4</sub>H<sub>10</sub>(2) mixture permeation across MFI membrane at 300 K. The values of  $S_{perm}$ are calculated from steady-state permeation simulations for the fluxes, taking  $p_{1\delta} = p_{2\delta} \approx 0$  and  $p_{10}/p_{20} =$ 95/5; see Figure 9a. We note that the highest selectivities in favor of *n*-butane is attained with  $D_1/D_{12}$ = 4, indicating large slowing-down effects.

Figures 9b, and 9c are plots of the normalized fluxes  $N_1/(\rho q_{10} D_1/\delta)$ , and  $N_2/(\rho q_{20} D_2/\delta)$  as a function of the total upstream pressure. We note that the normalized flux of n-butane is practically unaffected by the influence of correlations. On the other hand, the normalized flux of methane is reduced significantly with increasing values of  $D_1/D_{12}$ ; this illustrates the importance of correlation effects.

Slowing-down effects retard the mobility of H<sub>2</sub> in H<sub>2</sub>(1)/CO<sub>2</sub>(2) mixture permeation across MFI membranes, enhancing the separations in favor of CO<sub>2</sub>(2). In order to validate the M-S model equations to adequately describe mixture permeation across MFI membranes, Figure 10a,b compares the experimental data of Sjöberg et al.<sup>35</sup> for steady-state permeation of 50/50 equimolar H<sub>2</sub>(1)/CO<sub>2</sub>(2) mixtures across MFI (silicalite-1) zeolite membrane at 273 K with (steady-state) solutions to Equation (39), and (45) taking  $D_1/D_{12} = 20$  based on the MD data in Figure 8. There is excellent agreement between the Sjöberg data and the M-S model. The H<sub>2</sub>(1) flux is particularly sensitive to the choice of the parameter  $D_1/D_{12}$ . If correlations are completely neglected, and Equation (40) is used the H<sub>2</sub>(1) flux is severely over-predicted; see Figure 10b. In the other extreme, if we assume that correlations are dominant, i.e.  $D_1/D_{12} >>> 1$ , the following expression can be derived

$$\binom{N_1}{N_2} = \frac{\rho}{\frac{x_1}{D_1} + \frac{x_2}{D_2}} \begin{bmatrix} x_1 & x_1 \\ x_2 & x_2 \end{bmatrix} \begin{bmatrix} \Gamma_{11} & \Gamma_{12} \\ \Gamma_{21} & \Gamma_{22} \end{bmatrix} \begin{pmatrix} \frac{\partial q_1}{\partial r} \\ \frac{\partial q_2}{\partial r} \\ \frac{\partial q_2}{\partial r} \end{pmatrix}; \quad \text{correlations dominant}$$
(48)

The predictions of  $H_2(1)$  flux using Equation (48) provides the "lower limit" for the flux values. The simulation data in Figure 10a,b underscore the importance of proper modelling of correlation effects for MFI membrane permeation.

# 7. Simulation methodology for transient breakthrough in fixed bed adsorbers

Assuming plug flow of an *n*-component gas mixture through a fixed bed (see schematic in Figure 11) maintained under isothermal conditions, the partial pressures in the gas phase at any position and instant of time are obtained by solving the following set of partial differential equations for each of the species i in the gas mixture.<sup>6, 36</sup>

$$\frac{1}{RT}\frac{\partial p_i(t,z)}{\partial t} = -\frac{1}{RT}\frac{\partial (v(t,z)p_i(t,z))}{\partial z} - \frac{(1-\varepsilon)}{\varepsilon}\rho\frac{\partial \bar{q}_i(t,z)}{\partial t}; \quad i = 1,2,...n$$
(49)

In equation (49), t is the time, z is the distance along the adsorber,  $\rho$  is the framework density,  $\varepsilon$  is the bed voidage, v is the interstitial gas velocity, and  $\overline{q}_i(t,z)$  is the *spatially averaged* molar loading within the crystallites of radius  $r_c$ , monitored at position z, and at time t. The  $\overline{q}_i(t,z)$  is determined from Equations (30), (41), and (43).

In industrial practice, the most common operation is to use a step-wise input of mixtures to be separated into an adsorber bed that is initially free of adsorbates, i.e. we have the initial condition

$$t = 0; \quad q_i(0, z) = 0 \tag{50}$$

At time, t = 0, the inlet to the adsorber, z = 0, is subjected to a step input of the *n*-component gas mixture and this step input is maintained till the end of the adsorption cycle when steady-state conditions are reached.

$$t \ge 0; \quad p_i(0,t) = p_{i0}$$
 (51)

For presenting the breakthrough simulation results, we use the dimensionless time,  $\tau = \frac{tv}{L}$ , obtained

by dividing the actual time, t, by the characteristic time,  $\frac{L}{v}$ .

# 8. Transient CO<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> mixture uptake in DDR zeolite

DDR zeolite consists of cages, of 278 Å<sup>3</sup> size, separated by narrow windows.<sup>5, 37</sup> Figures 12, and 13 provide details of the pore landscape of DDR zeolite. Of crucial importance for diffusion are the dimensions of the windows connecting the cages; this information is summarized in Figure 14. The window dimensions are 3.65 Å × 4.37 Å. The framework density of DDR zeolite  $\rho = 1760$  kg m<sup>-3</sup>. Molecular Dynamics (MD) simulations<sup>25, 29, 38</sup> have established that CO<sub>2</sub> molecules jump lengthwise across the windows. The cross-section of a CO<sub>2</sub> molecule has a dimension of 3.03 Å, significantly lower than that of C<sub>2</sub>H<sub>6</sub> that has a cross section of 3.76 Å; see Figure 15. Using MD simulations<sup>25, 29, 38</sup> as guidelines, we anticipate the diffusivity of CO<sub>2</sub> to be about 1-3 orders of magnitude higher than that of C<sub>2</sub>H<sub>6</sub>.

Binder et al.<sup>39</sup> and Lauerer et al.<sup>40</sup> report a set of three mixture uptake experiments with 1:1, 2:1, and 3:1 partial pressure ratios for  $CO_2$  and  $C_2H_6$  in the gas phase. For modelling of the transient uptake of  $CO_2$  (= component 1) and  $C_2H_6$  (= component 2) within the DDR zeolite crystal, the first step in the simulations is to model mixture adsorption equilibrium.

The data on the unary isotherms of  $CO_2$  and  $C_2H_6$  at 298 K are provided in Figure 36, Chapter 4 of the PhD dissertation of Binder.<sup>41</sup> The unary isotherms for both  $CO_2$ , and  $C_2H_6$  can be described adequately by a single-site Langmuir isotherm

$$q_i = \frac{q_{i,sat}b_i p_i}{1 + b_i p_i} \tag{52}$$

The single-site Langmuir parameters are provided in Table 2; these fit parameters are on the basis of the scanned data from the PhD dissertation.

Figure 16 provides a comparison of unary isotherm data with single-site Langmuir fits using the parameters reported in Table 2. The fits are of good accuracy.

Figure 3 of Binder et al.<sup>39</sup> presents IAST calculations for binary mixture adsorption with constant CO<sub>2</sub> partial pressures of  $p_1 = 20$ , 40, and 60 kPa for experiments (1), (2), and (3), respectively. The partial pressures of C<sub>2</sub>H<sub>6</sub> ethane in the gas phase is varied. The IAST calculations of Binder et al.<sup>39</sup> are shown as symbols in Figure 17.

For the conditions of the Binder/Lauerer experiments,<sup>39, 40</sup> a good prediction of the mixture adsorption equilibrium is also provided by the mixed-gas Langmuir model. To demonstrate this, the calculations using the mixed-gas Langmuir model, equation (34) are presented as the continuous solid lines in Figure 17. For the range of experiments, the mixed-gas Langmuir model is in very good agreement with IAST calculations.

Since we have established the accuracy of the mixed-gas Langmuir model to describe  $CO_2/C_2H_6$ mixture adsorption equilibrium in DDR, the calculations using Equation (35) are justified, and accurate. Figure 18 presents calculations of elements of the matrix of thermodynamic correction factors  $\Gamma_{ij}$ , using Equation (35), expressed as a function of total mixture loading,  $q_t$ , for (a) 1:1, (b) 2:1, and (c) 3:1 ratios of partial pressures in the gas phase. In these calculations the total gas pressure,  $p_t$ , was varied from 1 to 100 kPa. The off-diagonal elements  $\Gamma_{12}$ , and  $\Gamma_{21}$  become increasingly important with increasing loadings. In particular, it is to be noted that the ratio  $\Gamma_{12}/\Gamma_{11}$  gets progressively closer to unity as the mixture loading increases. This implies that thermodynamic coupling effects are of particular importance for the uptake of CO<sub>2</sub> (1) from CO<sub>2</sub>(1)/C<sub>2</sub>H<sub>6</sub>(2) gas mixtures.

Figure 19 presents calculations of  $(\Gamma_{12} q_2/\Gamma_{11} q_1)$ , and  $(\Gamma_{21} q_1/\Gamma_{22} q_2)$  for binary CO<sub>2</sub>(1)/C<sub>2</sub>H<sub>6</sub>(2) mixture adsorption in DDR for 3:1 ratios of partial pressures in the gas phase. We note that  $(\Gamma_{12} q_2/\Gamma_{11} q_1)$  is significantly larger in magnitude than  $(\Gamma_{21} q_1/\Gamma_{22} q_2)$ . This implies that thermodynamic coupling effects influence CO<sub>2</sub> to a greater extent that C<sub>2</sub>H<sub>6</sub>.

A further point to emphasize about the data presented in Figure 18 and Figure 19 is that during transient desorption, the influence of the thermodynamic coupling effects should be expected to get less significant with time progression. We will see later, that this causes the adsorption/desorption trajectories to follow different trajectories in composition space.

If  $\mu_i^0$  is the chemical potential of species *i* at the standard state, then the quantities  $q_1(\mu_1 - \mu_1^0)/RT = \Gamma_{11}q_1 + \Gamma_{12}q_2$ , and  $q_2(\mu_2 - \mu_2^0)/RT = \Gamma_{21}q_1 + \Gamma_{22}q_2$  may be regarded as the "thermodynamically corrected" measures of component loadings of components 1 and 2. We will return to this point later in the discussions. At finite loadings, thermodynamic coupling effects cannot be ignored.

From Equation (40) we note that the intra-crystalline fluxes  $N_1$ , and  $N_2$  are, respectively, proportional to the gradients of the corrected loadings  $q_1(\mu_1 - \mu_1^0)/RT = \Gamma_{11}q_1 + \Gamma_{12}q_2$ , and  $q_2(\mu_2 - \mu_2^0)/RT = \Gamma_{21}q_1 + \Gamma_{22}q_2$ . In view of the calculations presented in Figure 19, we should expect the flux of CO<sub>2</sub> (= component 1) to be significantly influenced by the driving force of C<sub>2</sub>H<sub>6</sub> (= component 2).

In the Henry regime of adsorption, when the fractional occupancies are vanishingly small, we have the special case that the matrix of thermodynamic factors reduces to the identity matrix

$$\begin{bmatrix} \Gamma_{11} & \Gamma_{12} \\ \Gamma_{21} & \Gamma_{22} \end{bmatrix} \rightarrow \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}; \quad \theta_1, \theta_2 \rightarrow 0$$
(53)

If the thermodynamic coupling effects are neglected, and the elements of the matrix of thermodynamic factors  $\Gamma_{ij}$  equals Kronecker delta,  $\Gamma_{ij} = \delta_{ij}$  and we obtain the uncoupled form of the flux equations

$$\binom{N_1}{N_2} = -\rho \begin{bmatrix} D_1 & 0\\ 0 & D_2 \end{bmatrix} \begin{pmatrix} \frac{\partial q_1}{\partial r}\\ \frac{\partial q_2}{\partial r} \end{pmatrix}; \quad \text{neglecting thermodynamic coupling}$$
(54)

In the following discussions we shall compare the simulation using the flux relations (40), including thermodynamic coupling, with simulations using equation (54) that neglects thermodynamic coupling.

We simulated the three set of experiments reported by Binder/Lauerer,<sup>39, 40</sup>

Experiment 1: 1:1  $CO_2(1)/C_2H_6(2)$  bulk gas mixture at 298 K,  $p_1 = 20$  kPa,  $p_2 = 20$  kPa.

Experiment 2: 2:1 CO<sub>2</sub>(1)/C<sub>2</sub>H<sub>6</sub>(2) bulk gas mixture at 298 K,  $p_1 = 40$  kPa,  $p_2 = 20$  kPa.

Experiment 3: 3:1 CO<sub>2</sub>(1)/C<sub>2</sub>H<sub>6</sub>(2) bulk gas mixture at 298 K,  $p_1 = 60$  kPa,  $p_2 = 20$  kPa.

The hexagonal crystals of DDR zeolite (see Figure 20), used in the Binder/Lauerer experiments<sup>39, 40</sup> are modelled as spherical crystals of effective radius  $r_c$ .

The primary aim of our simulations is to trace the origins of the spatial and temporal overshoots in the uptake of CO<sub>2</sub>. The approach taken was to obtain a reasonably good match between the observed overshoot in the spatial-averaged uptake  $\overline{q}_i(t)$  vs time, t, data of Binder/Lauerer,<sup>39, 40</sup>

There are only two adjustable parameters in the simulations:  $D_1/r_c^2$ , and  $D_2/r_c^2$ . The parameter values that allowed good agreement between the experiments and simulations are listed below:

Experiment 1:  $D_1/r_c^2 = 0.125 \text{ s}^{-1}$ ;  $D_1/D_2 = 1333$ . See Figure 22.

Experiment 2:  $D_1/r_c^2 = 9.375 \times 10^{-3} \text{ s}^{-1}$ ;  $D_1/D_2 = 100$ . See Figure 23.

Experiment 3:  $D_1/r_c^2 = 6.25 \times 10^{-3} \text{ s}^{-1}$ ;  $D_1/D_2 = 50$ . See Figure 24.

Figure 21 presents plots of  $D_1/r_c^2$ , and  $D_2/r_c^2$ , for CO<sub>2</sub>(1), and C<sub>2</sub>H<sub>6</sub>(2) in DDR on the corresponding component loadings,  $q_1$ , and  $q_2$ , in the adsorbed phase at final equilibration. The component diffusivities appear to correlate with their loadings in the mixture, an expected trend.

The transient overshoot in the spatial-averaged uptake of  $CO_2$  is properly captured by the simulations of the Maxwell-Stefan model equation (40), including the influence of thermodynamic coupling; these set of simulations are shown by the continuous solid lines in Figure 22, Figure 23, are Figure 24. Also shown in Figure 22, Figure 23, are Figure 24 are comparisons of the simulations of the adsorption and desorption cycles, plotted in composition space. It is noteworthy that the composition adsorption/desorption trajectories follow completely different paths during equilibration. During desorption, the influence of the thermodynamic coupling effects become progressively less significant with time progression. Consequently, no undershoots are experienced during desorption.

If thermodynamic coupling effects are neglected and the uncoupled flux relation (54) is employed, then the overshoots time-averaged uptake of  $CO_2$  disappear, and both components approach equilibrium in a monotonous manner; see the dashed lines in Figure 22, Figure 23, are Figure 24.

We conclude that thermodynamic coupling effects are the root cause of the temporal overshoots of  $CO_2$ . The attainment of supra-equilibrium loadings within the DDR crystals signals the phenomenon of uphill transport. In order to investigate the genesis of uphill transport of  $CO_2$  we examine the spatial distribution of loadings within the crystal of DDR.

Figures 25, 26, and 27 present the simulation results, respectively for Experiments 1, 2, and 3, for the transient development of component loadings along the radius of DDR crystal (center, r = 0; surface of crystal,  $r = r_c$ ) monitored at different times from start of the uptake. During the transient equilibration, the loading of CO<sub>2</sub> exhibits spatial overshoots in all three Experiments 1, 2 and 3.

The spatial overshoot of CO<sub>2</sub> is a clear indication of uphill transport. What causes this uphill transport? In order to answer this question, we need to examine the mixture adsorption thermodynamics. Consider the simulations corresponding to Experiments 2, and 3. From the data on the  $q_1(r,t)$ , and  $q_2(r,t)$  we determined the quantities  $\Gamma_{11}q_1(r,t) + \Gamma_{12}q_2(r,t)$ , and  $\Gamma_{21}q_1(r,t) + \Gamma_{22}q_2(r,t)$  that are

thermodynamically corrected measures of component loadings of components 1 and 2. The radial profiles of these "corrected" loadings, are calculated using

$$\frac{\begin{pmatrix} q_1(\mu_1 - \mu_1^0) \\ q_2(\mu_2 - \mu_2^0) \end{pmatrix}}{RT} = \begin{bmatrix} \Gamma_{11} & \Gamma_{12} \\ \Gamma_{21} & \Gamma_{22} \end{bmatrix} \begin{pmatrix} q_1 \\ q_2 \end{pmatrix} = \frac{1}{1 - \theta_1 - \theta_2} \begin{bmatrix} 1 - \theta_2 & \frac{q_{1,sat}}{q_{2,sat}} \\ \frac{q_{2,sat}}{q_{1,sat}} \\ \theta_2 & 1 - \theta_1 \end{bmatrix} \begin{pmatrix} q_1 \\ q_2 \end{pmatrix}$$
(55)

Figure 28 shows the transient development of corrected loadings  $\Gamma_{11}q_1(r,t) + \Gamma_{12}q_2(r,t)$ , and  $\Gamma_{21}q_1(r,t) + \Gamma_{22}q_2(r,t)$  along the radius of DDR crystal for simulations of Experiment 2. In terms of corrected loadings, there is no spatial overshoot of CO<sub>2</sub>; this implies that CO<sub>2</sub> is not transported uphill of the gradient of its (partial) spreading pressure  $(A/RT)(\partial \pi_1/\partial r) = \Gamma_{11}(\partial q_1/\partial r) + \Gamma_{12}(\partial q_2/\partial r)$ .

Figure 29 shows the transient development of corrected loadings  $\Gamma_{11}q_1(r,t) + \Gamma_{12}q_2(r,t)$ , and  $\Gamma_{21}q_1(r,t) + \Gamma_{22}q_2(r,t)$  along the radius of DDR crystal for simulations of Experiment 3. In terms of corrected loadings, there is no spatial overshoot of CO<sub>2</sub>; this implies that CO<sub>2</sub> is not transported uphill of the gradient of its (partial) spreading pressure  $(A/RT)(\partial \pi_1/\partial r) = \Gamma_{11}(\partial q_1/\partial r) + \Gamma_{12}(\partial q_2/\partial r)$ .

This conclusion is further strengthened in the results presented in Figure 30 wherein the radial profiles of  $(\mu_1 - \mu_1^0)/RT$ , and  $(\mu_2 - \mu_2^0)/RT$  are plotted. The transient development of chemical potentials of the adsorbed components within the DDR crystal is monotonous. Diffusion of CO<sub>2</sub> is not uphill of its chemical potential gradient.

It now remains to demonstrate that the use of corrected loadings serves to rationalize the experimentally observed spatio-temporal overshoots in the CO<sub>2</sub> loadings in the Binder/Lauerer<sup>39, 40</sup> experiments. For this purpose, consider the IFM data on the radial profiles for uptake from 2:1  $CO_2/C_2H_6$  gas mixtures within the hexagonal crystals of DDR zeolite; the radial profiles for CO<sub>2</sub>, and  $C_2H_6$  loadings are reproduced in Figure 31. The overshoots in the CO<sub>2</sub> loadings during the transient approach to equilibration are analogous to those observed in the simulation results presented Figure 26. From the experimental data on the  $q_1(r,t)$ , and  $q_2(r,t)$  in Figure 31, we determined the quantities

 $\Gamma_{11}q_1(r,t) + \Gamma_{12}q_2(r,t)$ , and  $\Gamma_{21}q_1(r,t) + \Gamma_{22}q_2(r,t)$  that are thermodynamically corrected measures of component loadings of components 1 and 2; the results are presented in Figure 32. In terms of corrected loadings, there are no spatio-temporal overshoots for CO<sub>2</sub>. Indeed, the equilibration of both CO<sub>2</sub>, and C<sub>2</sub>H<sub>6</sub> proceeds in the same, conventional, manner. Both simulations (Figure 28), and experiments (Figure 32) confirm that the transport of CO<sub>2</sub> is downhill of the chemical potential gradient.

# 9. CO<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> separations in fixed bed DDR adsorber

The Binder/Lauerer uptake experiments suggest the possibility of diffusion-selective purification of ethane by selective removal of  $CO_2$  present as impurities. To demonstrate this possibility, we carried out transient breakthrough simulations in a fixed bed adsorber packed with crystallites of DDR.

Figure 33 shows the transient breakthrough of 10/90 CO<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> mixtures through fixed bed adsorber packed with DDR crystals operating at 298 K, and total pressure  $p_t = 100$  kPa. The parameter values are: L = 0.3 m; voidage of bed,  $\varepsilon = 0.4$ ; interstitial gas velocity, v = 0.1 m/s; radius of crystallite,  $r_c = 40$  $\mu$ m;  $D_1/r_c^2 = 0.00125$  s<sup>-1</sup>;  $D_1/D_2 = 1333$ . The y-axis is the gas phase concentration at the adsorber outlet, normalized with respect to the feed concentrations at the inlet. The x-axis is the dimensionless time,  $\tau = tv/L$ , obtained by dividing the actual time, t, by the characteristic time, L/v.

We note that  $C_2H_6$  breaks through earlier and can be recovered in purified form during the early stages of the transient operations. The separation relies on the significantly higher intra-crystalline diffusivity of CO<sub>2</sub>. If there is no intra-crystalline diffusional limitation, CO<sub>2</sub> breaks through earlier and the purification strategy will not work. The separation relies on the significantly higher diffusivity of CO<sub>2</sub>. If there is no intra-crystalline diffusional limitation, CO<sub>2</sub> breaks through earlier, and the purification strategy will be ineffectual.

### 10. Transient uptake of N<sub>2</sub>/CH<sub>4</sub> mixture in LTA-4A zeolite

The structural details for LTA-4A zeolite are shown in Figure 34.<sup>29</sup>

The Habgood<sup>42</sup> experimental data on transient mixture uptake, measured at 194 K with partial pressures  $p_1 = 50.9$  kPa and  $p_2 = 49.1$  kPa, are shown in Figure 35. The N<sub>2</sub>(1)/CH<sub>4</sub>(2) mixture constitutes ESI 28

a combination of more-mobile-less-strongly-adsorbed-N<sub>2</sub> and tardier-more-strongly-adsorbed-CH<sub>4</sub>. Nitrogen is a "pencil-like" molecule (4.4 Å  $\times$  3.3 Å) that can hop length-wise across the narrow windows; the "spherical" CH<sub>4</sub> (3.7 Å) is much more severely constrained and has a diffusivity that is 22 times lower than that of N<sub>2</sub>.

Table 3 provides the 1-site Langmuir parameters for  $N_2$  and  $CH_4$  in LTA-4A zeolite at 194 K.  $N_2$  has an adsorption strength that is a factor 2.2 lower than that of  $CH_4$ . The mixture adsorption equilibrium is described perfectly by the mixed-gas Langmuir equation (34).

During the initial stages of the transient uptake, the pores of LTA-4A are predominantly richer in the more mobile  $N_2$ , but this is displaced by the more strongly-adsorbed-but-tardier CH<sub>4</sub> molecules at longer times. This results in an overshoot in the  $N_2$  uptake in the experimental data. Note that the maximum loading of  $N_2$  is about a factor 2.5 times that of the final equilibrated uptake. Put another way, supra-equilibrium loadings are attained for  $N_2$  during a short time interval in the early stages of the transient uptake.

Let us now model the transient uptake process. The windows separating adjacent cages of LTA-4A zeolite are about 4 Å in size; each of the constituent species hops across the windows one-at-a-time. Put another way, the jumps are not correlated, and equations (40) can be used to describe intra-crystalline diffusion within crystals. The continuous solid lines in Figure 35 are the calculations using Equation (40). The simulations including thermodynamic coupling are able to quantitatively capture the overshoot in the spatial-averaged loading of N<sub>2</sub>. The parameter values used in the simulations are:  $D_1/r_c^2 = 1.56 \times 10^{-5} \text{ s}^{-1}$ ;  $D_2/r_c^2 = 7.2 \times 10^{-9} \text{ s}^{-1}$ .

The dashed lines in Figure 35 are the calculations using uncoupled flux equation (54). No overshoot is observed in this case. We concluded that thermodynamic coupling effects are the root cause of the overshoot in the spatial-averaged loading of  $N_2$ .

Also shown in Figure 35 are comparisons of the simulations of the adsorption and desorption cycles, plotted in composition space. The adsorption and desorption cycles follow completely different paths in

composition space; the rationalization is to be found in the influence of the thermodynamic factors. Also, no undershoots are experienced during desorption.

Figure 36 shows the transient development of N<sub>2</sub>(1), and CH<sub>4</sub>(2) loadings along the radius of LTA-4A crystal (center, r = 0; surface of crystal,  $r = r_c$ ) monitored at different times from start of the uptake. During the transient equilibration, the loading of N<sub>2</sub> exhibits spatial overshoots. The spatial overshoot of N<sub>2</sub> is a clear indication of uphill transport. From the data on the  $q_1(r,t)$ , and  $q_2(r,t)$  we determined the quantities  $\Gamma_{11}q_1(r,t) + \Gamma_{12}q_2(r,t)$ , and  $\Gamma_{21}q_1(r,t) + \Gamma_{22}q_2(r,t)$  that are thermodynamically corrected measures of component loadings of components 1 and 2. The radial profiles of these corrected loadings are shown in Figure 37. In terms of "corrected" loadings there is no spatial overshoot of N<sub>2</sub>; this implies that N<sub>2</sub> is not transported uphill of its thermodynamically "corrected" driving force  $\Gamma_{11}(\partial q_1/\partial r) + \Gamma_{12}(\partial q_2/\partial r)$ . In other words, the transport of N<sub>2</sub> is down its chemical potential gradient.

# 11. Transient uptake of O<sub>2</sub>/N<sub>2</sub> mixture in CMS

For  $O_2/N_2$  mixture separations, diffusion selectivity in favor of  $O_2$  is achievable by use of Carbon Molecular Sieve (CMS).<sup>43</sup> The mixed-gas Langmuir equation (34) is of good accuracy for description of mixture adsorption equilibrium; the unary isotherm data are provided in Table 4. The adsorption is in favor of  $N_2$ , whereas the diffusion favors  $O_2$ .

The experimental data of Chen et al.<sup>44</sup> for transient uptake of  $O_2/N_2$  mixture in CMS shows an overshoot for the more mobile  $O_2$ ; see Figure 38. The experimentally observed  $O_2$  overshoot is properly captured using the flux equations (40) with the ratio of diffusivities  $D_{O2}/D_{N2} = 36.8$ , based on the data provided by Chen et al.<sup>44</sup> If thermodynamic coupling is neglected, the  $O_2$  overshoot disappears.

Figure 39 shows the transient development of  $O_2(1)$ , and  $N_2(2)$  loadings along the radius of CMS particle (center, r = 0; surface of particles,  $r = r_c$ ) monitored at different times from start of the uptake. The more mobile  $O_2$  shows pronounced spatio-temporal overshoots during the transient approach to equilibrium.

## 12. Transient uptake of nC6/2MP mixture in MFI zeolite

Figures 40, and 41 provide the pore landscape and structural details of MFI zeolite.

The transient uptake of *n*-hexane(nC6)/2-methylpentane(2MP) mixtures in microporous crystals of MFI zeolite, exposed to an equimolar gas phase mixture at constant total pressure (= 2.6 Pa) have been reported by Titze et al.;<sup>45</sup> see Figure 42. The transient equilibration of nC6 displays a pronounced overshoot, achieving supra-equilibrium loadings during transient equilibration.

Titze et al.<sup>45</sup> have established the validity of the uncoupled M-S equations (40) to model intracrystalline fluxes by detailed consideration of correlation effects. The mixture adsorption equilibrium is determined using the IAST; the unary isotherm data are provided in Table 5. The essential features of the transient uptake on nC6/2MP uptake in MFI zeolite can be adequately captured by the flux equation (40) taking  $D_{nC6}/D_{2MP} = 100.^{45}$  The lower diffusivity of the mono-branched isomer 2MP is due to the severe configurational constraints within 5.5 Å sized channels of MFI. The nC6 overshoot is caused by the off-diagonal elements of [ $\Gamma$ ]. If we take  $\Gamma_{ij} = \delta_{ij}$ , the nC6 overshoot disappears.<sup>45</sup> The overshoot of nC6 signifies uphill diffusion within the crystals during transient equilibration; this phenomenon is advantageous in the PSA process for separation of hexane isomers, deployed in a process for octane enhancement of gasoline.<sup>6</sup>

There is one additional feature of nC6/2MP mixture uptake that distinguishes it from the  $CO_2/C_2H_6/DDR$ , N<sub>2</sub>/CH<sub>4</sub>/LTA-4A and O<sub>2</sub>/N<sub>2</sub>/CMS uptakes. For nC6/2MP/MFI both diffusion and adsorption favor the linear isomer; the two phenomena act in concert to enhance separations.<sup>6</sup>

Figure 43 shows the transient development of component loadings along the radius of MFI crystal (center, r = 0; surface of crystal,  $r = r_c$ ) monitored at different times from start of the uptake. The more mobile nC6 shows pronounced spatio-temporal overshoots during transient equilibration process. From the data on the  $q_1(r,t)$ , and  $q_2(r,t)$  we determined the quantities  $\Gamma_{11}q_1(r,t) + \Gamma_{12}q_2(r,t)$ , and  $\Gamma_{21}q_1(r,t) + \Gamma_{22}q_2(r,t)$  that are thermodynamically corrected measures of component loadings of components 1 and 2. The radial profiles of these corrected loadings are shown in Figure 44. In terms of corrected loadings there is no spatial overshoot of nC6; this implies that nC6 is not transported uphill of ESI 31

its thermodynamically corrected driving force  $\Gamma_{11}(\partial q_1/\partial r) + \Gamma_{12}(\partial q_2/\partial r)$ . In other words, the transport of nC6 is down its chemical potential gradient.

# 13. Transient uptake of n-C<sub>4</sub>H<sub>10</sub>/iso-C<sub>4</sub>H<sub>10</sub> in MFI zeolite

Figure 45 presents simulations of the transient uptake of n-butane(nC4)/iso-butane(iC4) mixtures in MFI. The linear *n*-butane has a mobility that is about 1-2 orders of magnitude higher than that of the branched isomer because of subtle configurational differences; this has been established PFG NMR experiments of Fernandez et al.<sup>46</sup> Configurational-entropy effects also serve to prefer the adsorption of the linear isomer.<sup>45</sup> There is synergy between adsorption and diffusion, analogous to that for nC6/2MP uptake. The continuous solid lines in Figure 45 are simulation results that include the influence of thermodynamic coupling. We note that the more mobile nC4 exhibits an overshoot. If the thermodynamic coupling effects are ignored, this overshoot disappears.

# 14. Transient uptake of benzene/ethylbenzene, and benzene/p-xylene in H-ZSM-5

The experimental data of Niessen and Karge<sup>47, 48</sup> for transient uptake of benzene(1)/ethylbenzene(2), and benzene(1)/p-xylene(2) mixtures in MFI zeolite (H-ZSM-5) show overshoots in the benzene uptake; see Figure **46** and Figure 47. The experimentally observed overshoots for benzene results from thermodynamic coupling effects; is demonstrated in the transient uptake simulations for the spatialaveraged component uptakes, that are also shown in Figure **46** and Figure 47.

#### 15. Transient uptake of n-heptane/benzene in NaX zeolite

The experimental data of Kärger and Bülow<sup>49</sup> for transient uptake of n-heptane(1)/benzene(2) mixture in NaX zeolite at 359 K shows an overshoot in the uptake of the more mobile n-heptane; see Figure **48**. Benzene is much more strongly adsorbed due to electrostatic interactions with the Na<sup>+</sup> cations. The stronger binding energy of benzene makes the mobility of benzene significantly lower than that of the non-polar n-heptane.<sup>50</sup> The windows separating the adjacent cages of NaX are about 7.4 Å, and correlations effects meed to be taken into consideration for quantitative modelling, and the

appropriate flux expressions Equation (39), including correlations are required.<sup>6, 25, 51</sup> However, correlation effects are not responsible for overshoots, as these tend to "iron out" differences between the species mobilities and mitigate against overshoots. The overshoot of the n-heptane uptake is solely ascribable to the off-diagonal elements of  $\begin{bmatrix} \Gamma_{11} & \Gamma_{12} \\ \Gamma_{21} & \Gamma_{21} \end{bmatrix}$ ; this is confirmed by the simulation results presented in Figure **48** that compares the calculations using Equation (40) with those obtained from uncoupled flux equation (54). We conclude that thermodynamic coupling cause overshoots of n-

#### 16. Transient uptake of N<sub>2</sub>/CH<sub>4</sub> in BaETS-4

heptane.

By tuning the size of the microporous channels and using ETS-4 as adsorbent, both adsorption and diffusion characteristics favor the selective uptake of  $N_2$  from  $N_2(1)/CH_4(2)$  mixtures.<sup>52-54</sup> The transient uptake data of Majumdar et al.<sup>53</sup> for Ba-ETS-4 are shown in Figures 49a, and 49b for (a) 10/90, and (b) 50/50 mixtures show overshoots in the uptake of the more mobile  $N_2$ . The pores of BaETS-4 virtually exclude methane molecules, and it is not entirely clear that the IAST calculations can be used to calculate mixture adsorption equilibrium; for this reason no simulation results are presented here to trace the origins of the nitrogen overshoots.

# 17. Transient uptake of hydrocarbon mixtures in Activated Carbon

Hu and Do<sup>55</sup> report experimental data for transient uptake of (a) ethane/n-butane, (b) ethane/npentane, and (c) n-butane/n-pentane mixtures in extrudates of activated carbon (AC) at 303 K; see Figures 8, 9, and 10 of their paper. In all three experiments, the more mobile species in the mixture exhibits an overshoot during equilibration. Figures 50a, b, c present our simulation results using the isotherm input data provided in Table 1 of Hu and Do.<sup>55</sup> The mixture adsorption equilibrium is determined using the IAST. The continuous solid lines using Equation (40) that include thermodynamic coupling effects. The dashed lines are simulations using uncoupled flux equation (54). In all three cases, overshoots are observed only when thermodynamic coupling effects are included. If thermodynamic coupling effects are ignored, i.e.  $\Gamma_{ij} = \delta_{ij}$ , no overshoots are observed.

Video animations for uptake of ethane/n-pentane mixture uptake, uploaded as ESI, demonstrate that the more mobile ethane exhibits spatio-temporal overshoots along the radius of the AC extrudate during its approach to equilibrium. Interestingly, Figure 11 of the paper by Hu and Do<sup>55</sup> also show similar overshoots, but these authors do not offer any explanation in terms of thermodynamic coupling effects.

The experimental data of Qiao and Hu<sup>56</sup> for transient uptake of ethane/propane mixtures in Ajax AC and Norrit AC show ethane overshoots in all of the reported experiments. The overshoot phenomena can be properly captured by using Equation (40) for the fluxes.

# 18. Influence of the ratio of M-S diffusivities, $\mathcal{D}_1/\mathcal{D}_2$ , on overshoots

From a practical standpoint, it is of interest to know under what set of conditions transient overshoots can be expect to occur. To get some insights into this question, we investigated binary  $C_3H_6(1)/C_3H_8(2)$ mixture uptake in ZIF-8. The pore landscape and structural details for ZIF-8 are provided in Figure 51, and Figure 52. In ZIF-8, the adsorption strength of the saturated propane is higher than that of propene. From the experimental isotherm data of Li et al.,<sup>57</sup> the ratio of single-site Langmuir parameter  $b_2/b_1 =$ 1.07 at 303 K. The windows of ZIF-8 have a dimension of about 3.3 Å. Due to subtle differences in bond lengths and bond angles (see Figures 53), the diffusivity of  $C_3H_6$  is higher than that of  $C_3H_8$ ; Li et al.<sup>57</sup> report the value of the ratio  $D_1/D_2 =$ 125 based on the data on pure component uptakes.

Figure 53 presents simulations of transient uptake of  $C_3H_6(1)/C_3H_8(2)$  mixture within crystals of ZIF-8, taking  $D_1/D_2 = 125$ . The more mobile propene exhibits a sharp overshoot in the uptake for simulations in which thermodynamic coupling is properly accounted for. If thermodynamic coupling effects are ignored, both  $C_3H_6$ , and  $C_3H_8$  display monotonous equilibration characteristics.

We undertook a parametric study to study the influence of the ratio of  $D_1/D_2$ . Three values for the ratio were chosen: 2, 10, and 125. In these three scenarios the diffusivity of the saturated alkane was held constant at the value  $D_2/r_c^2 = 1.2 \times 10^{-4} \text{ s}^{-1}$ . The results are presented in Figure 54. The overshoot

in the uptake of the unsaturated propene persists for the ratios  $D_1/D_2 = 10$  and  $D_1/D_2 = 125$ . However, for the choice  $D_1/D_2 = 2$ , the overshoot in the C<sub>3</sub>H<sub>6</sub> uptake is practically non-existent. We conclude that for overshoots to occur, the diffusivity of the more mobile partner species must be significantly higher than that of the partner species.

#### **19.** Demonstrating the possibility of transient undershoots

For separations in fixed beds, the adsorption cycle is followed by a desorption cycle. During desorption, there exists the possibility of undershoots in the loadings of the more mobile species. To demonstrate this possibility, Figure 55 presents simulations of transient desorption of  $C_3H_6(1)/C_3H_8(2)$  from crystals of ZIF-8 at 303 K. Initially, the crystals are equilibrated by exposing the crystals to bulk gas mixture with  $p_1 = 50$  kPa;  $p_2 = 50$  kPa. This equilibrated crystal is then brought into contact with a bulk gas phase with  $p_1 = 10$  kPa;  $p_2 = 10$  kPa. The continuous solid lines are transient uptake simulations use Equation (40). We note that the more mobile  $C_3H_6$  experiences an undershoot during transient desorption. The dashed lines are the calculations using uncoupled flux equation (54); in this scenario, no undershoot is detected.

# 20. Separating mono- and di-branched alkanes by exploiting uphill diffusion in MFI zeolite

The isomerization of alkanes, for the purposes of octane improvement, is a process of importance in the petroleum industry.<sup>6, 36, 58</sup> The product from the isomerization reactor, that commonly uses MOR or MFI zeolite as catalyst, consists of an equilibrium distribution of linear alkanes, mono-branched alkanes, and di-branched alkanes with carbon numbers in the 5-7 range. The values of the Research Octane Number (RON) increases with the degree of branching; for hexane isomers (n-hexane (nC6), 2-methylpentane (2MP), 3-methylpentane (3MP), 2,2-dimethylbutane (22DMB), 2,3-dimethylbutane (23DMB)) the RON values are as follows:. nC6 = 30, 2MP = 74.5, 3MP = 75.5, 22DMB = 94, 23DMB = 105. Therefore, di-branched isomers are preferred products for incorporation into the high-octane gasoline pool. The separation of di-branched 22DMB and 23DMB from linear nC6 can be achieved by

molecular sieving using, say, LTA-5A zeolite. The separation of di-branched isomers from monobranched isomers is much more challenging. An important strategy that is effective for this separation is the exploitation of uphill diffusion by using MFI zeolite.

As illustration of uphill diffusion we consider the separations of two different mixtures: (a) binary 2MP/22DMB gaseous mixture, and ternary 2-methylbutane (2MB)/2MP/22DMB gaseous mixtures. The chosen conditions for the separation correspond to the experimental data for, respectively, Run 17, and Run 20 of Jolimaître et al. that were conducted in a packed bed adsorber using MFI extrudates.<sup>59</sup> For each of these mixtures we perform transient uptake simulations within an MFI extrudate, along with transient breakthrough simulations for the packed bed adsorber. The adsorption and diffusivity data for MFI extrudates, reported by Jolimaître et al.,<sup>59, 60</sup> are summarized in Table 6. The adsorption hierarchy is 2MP > 22DMB > 2MB, whereas the diffusivity hierarchy is 2MB > 2MP >> 22DMB:  $D_{2MB}/r_c^2 = 7.5 \times 10^{-3} \text{ s}^{-1}$ ;  $D_{2MP}/r_c^2 = 5 \times 10^{-3} \text{ s}^{-1}$ ;  $D_{22DMB}/r_c^2 = 6.25 \times 10^{-5} \text{ s}^{-1}$ .

Consider first the transient uptake within MFI extrudates exposed to a gas phase 2MP/22DMB mixture at 473 K with the partial pressures of the components in the bulk gas phase are  $p_1 = 22.7$  kPa;  $p_2 = 26.6$  kPa. The continuous solid lines in Figure 56 represent the transient simulations that include thermodynamic coupling using the flux relations Equation (40); there is a pronounced overshoot in the uptake of 2MP. The dashed lines represent uptake simulations ignoring thermodynamic coupling and use uncoupled flux equation (54); no overshoot in 2MP uptake is observed. This leads us to conclude that thermodynamic coupling is the origin of the transient overshoot in the 2MP uptake.

Figure 57 shows the transient development of 2MP and 22DMB loadings along the radius of MFI extrudate (center, r = 0; surface of crystal,  $r = r_c$ ) monitored at different times from start of the uptake. The 2MP loading experiences spatio-temporal overshoots along the radius of the MFI extrudate. The 2MP loading peak traverses towards the centre of the extrudate as time progresses. Eventually the loadings are uniform over the entire radius of the extrudate.

Figure 58 shows the corresponding transient development of "corrected" loadings  $q_1(\mu_1 - \mu_1^0)/RT = \Gamma_{11}q_1 + \Gamma_{12}q_2$ , and  $q_2(\mu_2 - \mu_2^0)/RT = \Gamma_{21}q_1 + \Gamma_{22}q_2$  of 2MP, and 22DMB along the ESI 36
radius of MFI extrudate (center, r = 0; surface of crystal,  $r = r_c$ ) monitored at different times from start of the uptake. In terms of the corrected loadings, the transient equilibration of both 2MP and 22DMB occurs in a monotonous manner. This leads us to conclude that the transport of 2MP is down the gradient of its chemical potential.

Figure 59 presents a comparison of transient breakthrough experimental data (for Run 17) of Jolimaître et al.<sup>59</sup> with transient breakthrough simulations. There is good agreement between the transient breakthrough simulations, including thermodynamic coupling, with the experimental data.

Consider next the separation of a ternary gaseous 2-methylbutane (2MB)/2MP/22DMB mixture. Transient uptake inside MFI crystal exposed to a gas phase 2MB/2MP/22DMB mixture shows overshoots for the two mono-branched isomers 2MB, and 2MP; see Figure 60. If thermodynamic coupling effects are ignored, the component loadings of all three components exhibit monotonous approaches to equilibrium. Both mono-branched alkanes 2MB, and 2MP experience uphill diffusion that allows the attainment of supra-equilibrium loadings within MFI. As a consequence of uphill diffusion, the transient breakthrough experimental data (indicated by symbols in Figure 61) show the elution sequence 22DMB, 2MB, 2MP. This sequence is desirable, because the high-octane di-branched 22DMB can be recovered from the gas mixture exiting the adsorber in the initial transience, for incorporation into the gasoline pool.

The experimental breakthrough data are in good agreement with breakthrough simulations that takes take proper account of thermodynamic coupling, using the flux relations Equation (40); see continuous solid lines in Figure 61. If thermodynamic coupling effects are ignored (i.e. no uphill diffusion), the separation is less effective and is indicated by the dashed lines in Figure 61.

# 21. Separating linear alcohols by exploiting uphill diffusion in CHA zeolite

The experimental data of Saint-Remi et al.<sup>61</sup> for transient uptake of ethanol/1-propanol mixtures within SAPO-34, that is the structural analog of CHA zeolite, are shown in Figure 62. The more mobile ethanol is found to exhibit a pronounced maximum in the uptake transience. The mixture adsorption

equilibrium favors the shorter alcohol because of the higher packing efficiency of the shorter alcohol within the cages of SAPO-34.<sup>6, 62, 63</sup> The uphill diffusion of ethanol further assists in the preferential adsorption of the shorter alcohol. Indeed, as in the case of nC6/2MP uptake in MFI, both adsorption and diffusion phenomena favor the shorter chain alcohol. This adsorption-diffusion synergy can be exploited in fixed bed separations. The breakthrough experimental data of Remy et al.<sup>64</sup> for separation of ethanol/1-propanol mixtures in a fixed bed adsorber packed with SAPO-34, (Figure 63) shows that the component that is eluted first from the adsorber is the alcohol with the longer chain length. The efficacy of this separation relies on a combination of packing effects, and uphill diffusion.

Transient uptake simulation were performed for ethanol/1-propanol mixtures within CHA crystals, for which the data on pure component isotherms are available from Configurational-Bias Monte Carlo (CBMC) simulations; see Figure 64a. The Maxwell-Stefan diffusivities were chosen in the simulations are  $D_{ethanol}/r_c^2 = 4 \times 10^{-3} \text{ s}^{-1}$ ;  $D_{1-propanol}/r_c^2 = 4 \times 10^{-5} \text{ s}^{-1}$ . The continuous solid lines are transient uptake simulations use Equation (40). The dashed lines are the calculations using uncoupled flux equation (54); in this scenario, no ethanol overshoot is detected. The simulated uptake characteristics are in qualitative agreement with the experimental uptake data of Saint-Remi et al.<sup>61</sup> The more mobile ethanol exhibits spatio-temporal overshoots in the loadings, confirming that diffusion of ethanol occurs uphill its molar gradient; see Figure 64.

Transient breakthrough simulations (Figure 65) confirm that the component to be eluted first from the adsorber is the longer chain alcohol.

## 22. Transient C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> permeation across ZIF-8 membrane

For steady-state  $C_3H_6/C_3H_8$  permeation across ZIF-8 membrane, Pan et al.<sup>65</sup> and Liu et al.<sup>66</sup> report permeation selectivities in the range 30 – 35, strongly favoring the unsaturated alkene. Let us examine the transient membrane permeation characteristics. Figure 66 shows the results for simulation of transient permeation of  $C_3H_6(1)/C_3H_8(2)$  mixture across ZIF-8 membrane of thickness  $\delta = 10 \ \mu\text{m}$ . The partial pressures in upstream membrane compartment,  $p_{10} = p_{20} = 50 \ \text{kPa}$ . The downstream compartment is placed under vacuum, i.e.  $p_{1\delta} = p_{2\delta} \approx 0$ . As in the transient uptake simulations we take  $D_1/D_2 = 125$ . The simulation results are presented in terms of the normalized fluxes  $N_1/(\rho q_{10}D_1/\delta)$ , and  $N_2/(\rho q_{20}D_2/\delta)$  in which the loadings at the upstream face are:  $q_{10} = 1.937$  mol kg<sup>-1</sup>,  $q_{20} = 2.067$  mol kg<sup>-1</sup>. The continuous solid lines are the calculations using Equation (40). We note an overshoot in the flux of the alkene during early stages of the transience. If thermodynamic coupling effects are neglected, the C<sub>3</sub>H<sub>6</sub> flux overshoot disappears; see the dashed lines using uncoupled flux equation (54). These conclusions are precisely analogous to those reached on the basis of the transient uptake simulations presented in Figure 53.

The value of the permeation selectivity at steady-state,  $S_{\text{perm}} = 117$  for both scenarios, either including thermodynamic coupling or neglecting thermodynamic coupling. The membrane permeation experiments of Pan et al.<sup>65</sup> and Liu et al.<sup>66</sup> are consistent with the choice  $D_1/D_2 \approx 40$ .

Figure 67 shows the transient development of  $C_3H_6(1)$ , and  $C_3H_8(2)$  loadings along the membrane thickness (upstream face, z = 0; downstream face,  $z = \delta$ ) monitored at different times from start of the permeation. The loading of C3H6 shows an overshoot in the transient approach to steady-state; this signifies uphill diffusion across the membrane. In terms of corrected loadings  $q_1(\mu_1 - \mu_1^0)/RT = \Gamma_{11}q_1 + \Gamma_{12}q_2$ , and  $q_2(\mu_2 - \mu_2^0)/RT = \Gamma_{21}q_1 + \Gamma_{22}q_2$  the loading profiles of both C<sub>3</sub>H<sub>6</sub>(1), and  $C_3H_8(2)$  display monotonous characteristics; see Figure 68. This indicates that membrane permeation is downhill of the chemical potential gradient.

#### 23. Transient CH<sub>4</sub>/nC<sub>4</sub>H<sub>10</sub> permeation across MFI membrane

Geus et al.<sup>67</sup> report experimental data on transient permeation 50/50 CH<sub>4</sub>/nC<sub>4</sub>H<sub>10</sub> mixture across an MFI membrane. The flux of the more mobile CH<sub>4</sub> exhibits a pronounced overshoot during transient approach to steady state; see Figure 69a. We performed transient simulations to capture the experimentally observed overshoots. Unlike all of the simulations discussed in the foregoing sections, the proper modelling of mixture diffusion of light hydrocarbons in MFI zeolite requires us to take proper account of correlation effects.<sup>25</sup> We need to take account of both correlations and thermodynamic

coupling using Equation (39). On the basis of the MD simulation data in Figure 8, and the permeation selectivity calculations in Figure 9, we take  $D_1/D_{12} = 2$  as a good estimate of the degree of correlations based on the mixture loadings at the upstream face of the membrane.

Figure 69b shows the shows the normalized fluxes  $N_1/(\rho q_{10}D_1/\delta)$ , and  $N_2/(\rho q_{20}D_2/\delta)$  as a function of the square root of time. The continuous solid lines in Figure 69b are the calculations using Equation (39), including both correlations and thermodynamic coupling. Also shown are simulations using Equation (40) that include thermodynamic coupling but neglect correlations. Including correlation effects tends to smear out the magnitude of the overshoots. In other words, correlation effects cannot cause overshoots. The dashed lines in Figure 69b are the calculations using uncoupled flux equation (54). The overshoot in the methane flux is essentially captured by both the M-S Equation (39) and Equation (40). If both correlations, and thermodynamic coupling effects are neglected, the overshoot in CH<sub>4</sub> flux disappears.

Figure 70 shows the transient development of  $CH_4(1)$ , and  $nC_4H_{10}(2)$  loadings along the MFI membrane thickness (upstream face, z = 0; downstream face,  $z = \delta$ ) monitored at different times from start of the permeation. The loading of the more mobile  $CH_4$  shows spatio-temporal overshoots during the approach to steady-state.

In terms of corrected loadings  $q_1(\mu_1 - \mu_1^0)/RT = \Gamma_{11}q_1 + \Gamma_{12}q_2$ , and  $q_2(\mu_2 - \mu_2^0)/RT = \Gamma_{21}q_1 + \Gamma_{22}q_2$  the loading profiles of CH<sub>4</sub>(1), and nC<sub>4</sub>H<sub>10</sub>(2) display monotonous characteristics; see Figure 71. This indicates that CH<sub>4</sub> membrane permeation is downhill of the chemical potential gradient.

### 24. Transient H<sub>2</sub>/nC<sub>4</sub>H<sub>10</sub> permeation across MFI membrane

The experimental data of Bakker<sup>68</sup> for transient permeation  $H_2/nC_4H_{10}$  mixture across an MFI membrane shows a maximum in the flux of the more mobile  $H_2$ ; see Figure 72a. Since the mobility of  $H_2$  is about two orders of magnitude higher than that of  $nC_4H_{10}$ , the overshoot in the  $H_2$  flux is very prominent.

From the data in Figure 9, we use  $D_1/D_{12} = 5$  as a good estimate of the degree of correlations. The continuous solid lines in Figure 72b are the calculations using Equation (39), including both correlations and thermodynamic coupling. The plot shows the normalized fluxes  $N_1/(\rho q_{10}D_1/\delta)$ , and  $N_2/(\rho q_{20}D_2/\delta)$  as a function of the square root of time. The dashed lines are the calculations using uncoupled flux equation (54). The overshoot in the hydrogen flux is adequately captured by the M-S Equation (39). If both correlations, and thermodynamic coupling effects are neglected, the overshoot in H<sub>2</sub> flux disappears.

Figure 73 shows the transient development of  $H_2(1)$ , and  $nC_4H_{10}(2)$  loadings along the MFI membrane thickness (upstream face, z = 0; downstream face,  $z = \delta$ ) monitored at different times from start of the permeation. The loading of the more mobile  $H_2$  shows spatio-temporal overshoots during the transient approach to steady-state.

In terms of corrected loadings  $q_1(\mu_1 - \mu_1^0)/RT = \Gamma_{11}q_1 + \Gamma_{12}q_2$ , and  $q_2(\mu_2 - \mu_2^0)/RT = \Gamma_{21}q_1 + \Gamma_{22}q_2$  the loading profiles of H<sub>2</sub>(1), and nC<sub>4</sub>H<sub>10</sub>(2) display monotonous characteristics; see Figure 74. This indicates that H<sub>2</sub> membrane permeation is downhill of the chemical potential gradient.

#### 25. Transient nC6/2MP permeation across MFI membrane

For permeation of nC6/2MP, and nC6/2,3dimethylbutane (23DMB) mixture across an MFI membrane, Matsufuji et al.<sup>69</sup> have reported experimental data showing overshoots in the nC6 flux during transient approach to steady-state; see Figures 75a, and 75b. For a rationalization and understanding of the nC6 overshoots, we carried out performed a set of simulations. Figure 76 shows the simulation results for transient permeation of nC6(1)/2MP(2) mixture across MFI membrane of thickness  $\delta = 50 \ \mu\text{m}$  at 300 K. The partial pressures in upstream membrane compartment,  $p_{10} = p_{20} = 1.3$  Pa, corresponding to the Titze uptake experiment. The plots in Figure 76 show the normalized fluxes  $N_1/(\rho q_{10} D_1/\delta)$ , and  $N_2/(\rho q_{20} D_2/\delta)$  as a function of the square root of time. The linear alkane displays an overshoot during transient approach to steady-state. If thermodynamic coupling effects are neglected, the nC6 flux overshoot disappears; see the dashed lines using uncoupled flux equation (54).

These conclusions are precisely analogous to those reached on the basis of the transient uptake simulations presented in Figure 42.

Figure 77 shows the transient development of nC6(1), and 2MP(2) loadings loadings along the membrane thickness (upstream face, z = 0; downstream face,  $z = \delta$ ) monitored at different times from start of the permeation. The loading of nC6 shows an overshoot in the transient approach to steady-state; this signifies uphill diffusion of nC6 across the membrane. In terms of corrected loadings  $q_1(\mu_1 - \mu_1^0)/RT = \Gamma_{11}q_1 + \Gamma_{12}q_2$ , and  $q_2(\mu_2 - \mu_2^0)/RT = \Gamma_{21}q_1 + \Gamma_{22}q_2$  the loading profiles of nC6(1), and 2MP(2) display monotonous characteristics; see Figure 78. This indicates that nC6 membrane permeation is downhill of the chemical potential gradient.

#### 26. Transient xylenes permeation across MFI membrane

The experimental data of Matsufuji et al.<sup>70</sup> for transient permeation of (a) 50/50 m-xylene/p-xylene, and (b) 24/51/25 p-xylene/m-xylene/o-xylene mixtures across MFI membrane show a maximum in the flux of p-xylene which is the most mobile of the three xylene isomers; see Figures 79a, and 79b. The most likely cause of this maximum is the influence of thermodynamic coupling. To verify this conclusion we carried out simulations of transient membrane for 50/50 m-xylene/p-xylene mixtures across an MFI membrane. O-xylene and m-xylene locate preferentially at the intersections of MFI, whereas the linear p-xylene molecules align the channels; see snapshots in Figure 79. The pure component isotherms, obtained from CBMC simulations,<sup>71</sup> show that, up to a loading of 4 molecules per unit cell the guest molecules are located at the channel intersections. At these locations, the adsorption strength of m-xylene is higher than that of p-xylene; this is due to more optimal interactions with the framework atoms. Para-xylene has the higher mobility because it has a more slender configuration allowing higher mobility along the intersecting channel topology of MFI zeolite. Transient uptake simulation results for two different scenarios are presented in Figure 80. Inclusion of thermodynamic coupling effects (continuous solid lines), and use of the flux equations (40) produces a maximum in the flux of the more mobile p-xylene during the early stages of the transience. Use the using uncoupled flux equation (54), ignoring thermodynamic coupling (dashed lines), with  $\Gamma_{ij} = \delta_{ij}$ , results in a monotonous approach to steady-state for both components. It must be remarked that Matsufuji et al.<sup>70</sup> offer the explanation that the maximum in the flux of p-xylene is caused due to "blocking" of the transport of p-xylene in the later stages of the transience due to increasing occupation of the channels by the more strongly adsorbed m-xylene and o-xylene. Our belief, based on the presented simulations evidence, is that the maximum is ascribable to the influence of thermodynamic coupling.

### 27. Transient nC4/iC4 permeation across MFI membrane

For nC4/iC4 mixture permeation across a MFI membrane, curious overshoots, and undershoots, in the transient retentate and permeate concentrations have been reported in the experiments of Courthial et al.<sup>72</sup> Figure 81 present simulation of transient permeation of 5/95 nC4(1)/iC4(2) mixtures across a MFI membrane at 300 K. When thermodynamic coupling effects are included, the flux of nC4 exhibits a pronounced overshoot. This overshoot disappears if thermodynamic coupling effects are neglected. We conclude that the overshoots observed in the experiments of Courthial et al.<sup>72</sup> are ascribable to thermodynamic coupling.

# 28. Transient water/ethanol permeation across DDR, and LTA-4A membrane

Pervaporation of water/alcohol mixtures is an important process in the processing industry, and a wide variety of membrane materials has been used, including polymers, zeolites (e.g. CHA, LTA, MFI, FAU, DDR), ZIF-8, and mixed matrix membranes.<sup>73-76</sup> Due to the high mobility of water molecules, uphill transport of water is to be expected during the transient approach to steady-state.

In order to demonstrate the possibility of uphill diffusion, we carried out a set of membrane permeation simulations for 5/95 water/ethanol mixtures across a DDR membrane; see Figure 82. The water diffusivity is taken to be 10 times that of ethanol diffusivity in the mixture. Simulations including

thermodynamic coupling show pronounced overshoot in the water flux. If thermodynamic coupling is neglected, the transient approach to steady-state occurs in a monotonous manner.

Figure 83 shows the water(1), and ethanol(2) loading across the DDR membrane thickness (upstream face, z = 0; downstream face,  $z = \delta$ ) monitored at different times from start of the permeation. The spatio-temporal overshoot in the water loading is a clear indication of uphill transport.

Figure 84, and Figure 85 show the corresponding results for 5/95 water/ethanol pervaporation across LTA-4A membrane; these calculations are based on the isotherm data of Pera-Titus et al.<sup>77</sup> The conclusions that emerge are analogous to those reached for DDR membrane pervaporation.

#### 29. Transient overshoots for alkane isomerization using MFI catalyst

In all of the examples considered in the foregoing, no formation or destruction of components were assumed to occur as a result of chemical reactions. We now demonstrate the possibility of transient overshoots with microporous catalysts. The phenomena involve an interplay between mixture adsorption, microporous diffusion and chemical reaction. For illustration, we restrict our analysis to a reversible isomerization reaction  $A_1 \leftrightarrow A_2$ ; such isomerization reactions are of great significance to the petroleum industry.<sup>21-23, 78-81</sup> Let us consider the specific example of isomerization of 2-methylpentane (2MP) to its dibranched isomer 2,2 dimethylbutane (22DMB) in a packed bed reactor using extrudates of MFI zeolite as catalyst. The process conditions correspond to those used in Run 17 by Jolimaître et al.,<sup>59, 60</sup> that are summarized in Table 6. The rate of chemical reaction,  $2MP(1) \rightleftharpoons 22DMB(2)$ , expressed as moles per kg of catalyst per second, is written as

$$Rate = k_1 q_1 - k_2 q_2 \tag{56}$$

The mixed-gas Langmuir model for mixture adsorption equilibrium, equation (34), relates the molar loadings of components 1 (= 2MP) and 2 (= 22DMB) to the partial pressures  $p_1$  and  $p_2$  in the bulk gas phase surrounding the MFI catalyst. The reaction rate constants, taken from Baur and Krishna,<sup>21</sup> are  $k_1 = 0.0011 \text{ s}^{-1}$ ,  $k_2 = 0.00055 \text{ s}^{-1}$ .

The radial distribution of molar loadings,  $q_i$ , within a spherical MFI extrudate catalyst, of radius  $r_c$ , is obtained from a solution of a set of differential equations describing the uptake

$$\frac{\partial q_i(r,t)}{\partial t} = -\frac{1}{\rho} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 N_i \right) + \rho v_i Rate$$
(57)

where  $v_i$  is the reaction stoichiometric coefficient;  $v_1 = -1$  for reactant 2MP;  $v_2 = 1$  for product 22DMB.

The fluxes  $N_i$ , in turn, are related to the radial gradients in the molar loadings by Equation (40). At time t = 0, i.e. the initial conditions, the molar loadings  $q_i(r,0)$  at all locations r within the catalyst are uniform (zero loadings). For all times  $t \ge 0$ , the exterior of the crystal is brought into contact with a bulk gas mixture at partial pressures  $p_i(r_c,t)$  that is maintained constant till the crystal reaches thermodynamic equilibrium with the surrounding gas mixture. At any time t, during the transient approach to thermodynamic equilibrium, the spatial-averaged component loading within the crystallites

of radius 
$$r_c$$
 is calculated using  $\overline{q}_i(t) = \frac{3}{r_c^3} \int_0^{r_c} q_i(r,t) r^2 dr$ .

The numerical details are provided on our website.<sup>33</sup>

Before proceeding to transient uptake simulations, let us analyze the influence of intra-crystalline diffusion on the isomerization reaction under steady-state conditions for which we have

$$\frac{1}{\rho} \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 N_i) = -\rho v_i Rate; \quad \text{steady-state}$$
(58)

After insertion of the appropriate rate expressions for the chemical reaction rate, *Rate*, and the flux equations for  $N_i$ , the equation (58) can be solved to obtain the steady-state distribution of the loadings of the components along the crystal radius, *r*.

$$\eta = \frac{\int_{0}^{1} Rate(r/r_{c})^{2} d(r/r_{c})}{\int_{0}^{1} Rate|_{r=r_{c}}(r/r_{c})^{2} d(r/r_{c})}$$
(59)

The chemical reaction rate, *Rate* defined in equation (56), varies with loading and *r*-dependent. The effectiveness factor,  $\eta$ , quantifies the influence of intra-crystalline diffusion on the effective rate of chemical reaction. In the absence of any diffusional limitations,  $\eta = 1$ , and the chemical reaction rate can be calculated using the loadings at the external surface, *Rate* $|_{r=r_c}$ .

Baur and Krishna.<sup>21</sup> have presented analytic solutions to equation (58) for a variety of scenarios.

- (1) Classical scenario: the diffusivities are independent of loading (called the weak confinement scenario), and thermodynamic coupling effects are ignored,  $\Gamma_{ij} = \delta_{ij}$ . Also ignored are the correlation effects, i.e.  $D_1/D_{12} \rightarrow 0$ ;  $D_2/D_{12} \rightarrow 0$ .
- (2) Weak confinement scenario for the diffusivities. Also ignored are the correlation effects, i.e.  $D_1/D_{12} \rightarrow 0; \quad D_2/D_{12} \rightarrow 0$ . Thermodynamic coupling effects are accounted for using the mixedgas Langmuir isotherm model
- (3) Strong confinement scenario for the diffusivities in which the diffusivities are related to the zeroloading diffusivities by  $D_i = D_i(0)\theta_V$ . Also ignored are the correlation effects, i.e.  $D_1/D_{12} \rightarrow 0$ ;  $D_2/D_{12} \rightarrow 0$ . Thermodynamic coupling effects are accounted for using the mixedgas Langmuir isotherm model
- (4) Weak confinement scenario for the diffusivities. Thermodynamic coupling effects are accounted for using the mixed-gas Langmuir isotherm model. Correlation effects are accounted for with finite values of  $D_1/D_{12}$ ;  $D_2/D_{12}$
- (5) Strong confinement scenario for the diffusivities in which the diffusivities are related to the zeroloading diffusivities by  $D_i = D_i(0)\theta_V$ . Thermodynamic coupling effects are accounted for using the mixed-gas Langmuir isotherm model. Correlation effects are accounted for with finite values of  $D_1/D_{12}$ ;  $D_2/D_{12}$

For the classical scenario (1), the effectiveness factor is given by

$$\eta = \frac{1}{\phi} \left( \frac{1}{\tanh(3\phi)} - \frac{1}{(3\phi)} \right); \quad \text{classical scenario}(1)$$
(60)

where the Thiele modulus is calculated from

$$\phi = \frac{r_c}{3} \sqrt{\frac{k_1}{D_1(0)} + \frac{k_2}{D_2(0)}}$$
(61)

Analytical solutions are derived for the other four scenarios by Baur and Krishna<sup>21</sup> and the results for the effectiveness factor are expressed as

$$\eta = \frac{1}{\Phi} \left( \frac{1}{\tanh(3\Phi)} - \frac{1}{(3\Phi)} \right); \quad \text{General scenario}$$
(62)

where the generalized Thiele modulus  $\Phi$  is obtained by multiplying the classical Thiele modulus  $\phi$  by various "correction factors" as listed in Table 13.<sup>21</sup>

As illustration, Figure 86 presents calculations of the (steady-state) effectiveness factor,  $\eta$ , for uptake inside MFI catalyst exposed to a gas phase 2MP(1)/22DMB(2) mixture at 473 K, carrying out the isomerization reaction 2MP(1) $\rightleftharpoons$ 22DMB(2). The partial pressures of the components in the bulk gas phase are  $p_1 = 22.7$  kPa;  $p_2 = 26.6$  kPa. The ratio of rate constants  $k_1/k_2 = 2$ . The values of the rate constant  $k_1$  are varied. The zero-loading diffusivities  $D_1(0) = 2 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ ;  $D_1(0) = 2.5 \times 10^{-16} \text{ m}^2 \text{ s}^{-1}$ . The radius of the crystal  $r_c = 2 \mu \text{m}$ . The *x*-axis in Figure 86 is the classical Thiele modulus calculated using equation (61). The calculations using the five different scenarios are based on the analytical solutions provided by Baur and Krishna;<sup>21</sup> for scenarios (4) and (5) the correlation effects are quantified taking  $D_1/D_{12} = 1$ ;  $D_2/D_{12} = 0.0125$ . The highest effectiveness factors are obtained with the classical scenario in which thermodynamic coupling effects are ignored, by taking  $\Gamma_{ij} = \delta_{ij}$ . As is to be expected, diffusion effects are strongest for the scenarios in which the M-S diffusivities are linearly related to the vacancies,  $D_i = D_i(0)\theta_V$ . For the choice  $D_1/D_{12} = 1$ ;  $D_2/D_{12} = 0.0125$ , the influence of correlation effects is negligible. In all the transient simulations for uptake in MFI catalyst considered below, we compare the results obtained from the classical scenario 1 (neglecting thermodynamic coupling) with that of scenario 2 (including thermodynamic coupling). The equilibrated loadings inside the catalyst will be different in these two scenarios; we return to this point later.

Consider first the transient uptake with chemical reaction within MFI extrudates exposed to a gas phase 2MP/22DMB mixture at 473 K with the partial pressures of the components in the bulk gas phase are  $p_1 = 22.7$  kPa;  $p_2 = 26.6$  kPa. The continuous solid lines in Figure 87 represent the transient simulations that include thermodynamic coupling using the flux relations Equation (40); there is a pronounced overshoot in the uptake of 2MP. The dashed lines represent uptake simulations ignoring thermodynamic coupling and use uncoupled flux equation (54); no overshoot in 2MP uptake is observed. This leads us to conclude that thermodynamic coupling is the origin of the transient overshoot in the 2MP uptake.

Figure 88 shows the transient development of 2MP and 22DMB loadings along the radius of MFI catalyst (center, r = 0; surface of crystal,  $r = r_c$ ) monitored at different times from start of the uptake. The 2MP loading experiences spatio-temporal overshoots along the radius of the MFI extrudate. The 2MP loading peak traverses towards the centre of the extrudate as time progresses. Eventually the loadings are uniform over the entire radius of the extrudate.

Figure 89 shows the corresponding transient development of "corrected" loadings  $q_1(\mu_1 - \mu_1^0)/RT = \Gamma_{11}q_1 + \Gamma_{12}q_2$ , and  $q_2(\mu_2 - \mu_2^0)/RT = \Gamma_{21}q_1 + \Gamma_{22}q_2$  of 2MP, and 22DMB along the radius of MFI catalyst (center, r = 0; surface of crystal,  $r = r_c$ ) monitored at different times from start of the uptake. In terms of the corrected loadings, the transient equilibration of both 2MP and 22DMB occurs in a monotonous manner. This leads us to conclude that the transport of 2MP is down the gradient of its chemical potential.

Figure 90 presents the transient breakthrough simulations for fixed bed 2MP/22DMB isomerization reactor with MFI extrudates. The continuous solid lines represent breakthrough simulations include

thermodynamic coupling using the flux relations Equation (40). The dashed lines represent breakthrough simulations ignoring thermodynamic coupling and using uncoupled flux equation (54).

Consider uptake within MFI catalyst carrying out the isomerization of nC6 to produce a product containing mono-branched 3-methylpentane (3MP) and di-branched 22DMB. We restrict our analysis to the simplified reaction scheme

$$nC6(1) \not\ge 3MP(2) \not\ge 22DMB(3)$$
 (63)

where the Langmuir-Hinshelwood (LH) reaction rate expressions for the two constituent reversible reactions, expressed as moles per m<sup>3</sup> catalyst per second are

$$Rate_{1} = (k_{f1}p_{1} - k_{b1}p_{2})\theta_{V}; \quad Rate_{2} = (k_{f2}p_{2} - k_{b2}p_{3})\theta_{V}; \quad \theta_{V} = 1 - \theta_{1} - \theta_{2}$$
(64)

where the subscripts f and b refer to the forward and reverse reactions, and the subscripts 1 and 2 refer to the first and second isomerization reaction steps in Eq. (63). From available information for the free energies of formation<sup>28</sup> we can estimate the values of the equilibrium constants  $k_{f1}/k_{b1}$  and  $k_{f2}/k_{b2}$ . On the basis of this information, along with data on reaction kinetics<sup>82</sup> we take  $k_{f1} = k_{f2} = 0.009$  mol m<sup>-3</sup> Pa<sup>-1</sup> s<sup>-1</sup> and  $k_{b1} = k_{b2} = 0.007$  mol m<sup>-3</sup> Pa<sup>-1</sup> s<sup>-1</sup>. Further details of the kinetics are provided by Krishna and Baur.<sup>81</sup> The catalyst radius is taken to be  $r_c = 100 \mu m$ .

Figure 91 presents simulations of transient uptake inside MFI catalyst exposed to a gas phase nC6(1)/3MP(2)/22DMB(3) mixture at 362 K. nC6(1) $\rightleftharpoons$  3MP(2) $\rightleftharpoons$  22DMB(3). The partial pressures of the components in the bulk gas phase are  $p_1 = 2$  kPa;  $p_2 = 40$  kPa,  $p_3 = 60$  kPa. Diffusional effects are quantified with  $D_{nC6}/r_c^2 = 2 \times 10^{-2}$  s<sup>-1</sup>,  $D_{3MP}/r_c^2 = 2 \times 10^{-3}$  s<sup>-1</sup>;  $D_{22DMB}/r_c^2 = 1 \times 10^{-3}$  s<sup>-1</sup>. All three M-S diffusivities are assumed to follow the loading dependence  $D_i(\theta) = D_i(0)\theta_V$ . The continuous solid lines represent uptake simulations include thermodynamic coupling using the flux relations (40). We note that the most mobile nC6 displays an overshoot during transient uptake. The dashed lines represent

uptake simulations ignoring thermodynamic coupling and use uncoupled flux equation (54); in this scenario, nC6 approaches equilibrium in a monotonous manner.

#### **30.** Transient overshoots for xylene isomerization using MFI catalyst

Para-xylene is an important feedstock in the petrochemical industry.<sup>63</sup> The largest use of p-xylene is in its oxidation to make terephthalic acid, that is used in turn to make polymers such as polyethylene terephthalate (PET) and polybutylene terephthalate (PBT). PET is one of the largest volume polymers in the world, and is used to produce fibers, resins, films, and blown beverage bottles. Isomerization of xylenes with MFI catalyst is of importance.

For illustration, we consider the isomerization of m-xylene to p-xylene: m-xylene(1) $\rightleftharpoons p-xy$ lene(2). The rate of chemical reaction, expressed as moles per kg of catalyst per second is written as  $Rate = k_1q_1 - k_2q_2$ . The rate constants are taken as:  $k_1 = 0.001$  s<sup>-1</sup>,  $k_2 = 0.0005$  s<sup>-1</sup>. Unlike the example of the 2MP(1) $\rightleftharpoons$ 22DMB(2) reaction considered in a foregoing section, p-xylene has a higher diffusivity than m-xylene due to configurational considerations. We assume that the diffusivity of p-xylene is five times that of m-xylene.

Figure 92 shows the transient uptake inside MFI catalyst exposed to a gas phase m-xylene(1)/pxylene(2) mixture at 303 K. The partial pressures of the components in the bulk gas phase are  $p_1 = 10$ Pa;  $p_2 = 10$  Pa. The continuous solid lines represent uptake simulations include thermodynamic coupling using the flux relations Equation (40). In this scenario, we note that p-xylene shows a pronounced overshoot in the uptake. The dashed lines represent uptake simulations ignoring thermodynamic coupling and use uncoupled flux equation (54); in this scenario no m-xylene overshoot is observed.

#### 31. Transient overshoots for ethylation of benzene using MFI catalyst

H-ZSM-5, which has the MFI topology, is used as a catalyst for carrying out the ethylation of benzene

to produce ethylbenzene ethene(1)+benzene(2) ≥ ethylbenzene(3); for background on process and

reaction kinetics, see Hansen et al.<sup>83, 84</sup> For feed mixtures with ethene/benzene far in excess of the stoichiometric ratio of 1:1, we may assume that the rate of chemical reaction, expressed as moles per kg of catalyst per second, is written as

$$Rate = k_f q_2 - k_b q_3 \tag{65}$$

Using the data in the papers of Hansen et al.<sup>83, 84</sup> as guidelines for the kinetics, we take  $k_f = 1 \times 10^{-2} \text{ s}^{-1}$ and  $k_b = 5 \times 10^{-3} \text{ s}^{-1}$ .

Figure 93 presents the simulation results for transient uptake inside MFI catalyst exposed to a gas phase ethene(1)/benzene(2)/ethylbenzene(3) mixture at 653 K; the partial pressures of the components in the bulk gas phase are  $p_1 = 800$  kPa;  $p_2 = 200$  kPa;  $p_3 = 0$  kPa. Diffusional effects are quantified with  $D_{ethene}/r_c^2 = 1 \times 10^{-3} \text{ s}^{-1}$ ,  $D_{benzene}/r_c^2 = 2 \times 10^{-5} \text{ s}^{-1}$ ;  $D_{ethylbenzene}/r_c^2 = 1 \times 10^{-5} \text{ s}^{-1}$ . The continuous solid lines represent uptake simulations include thermodynamic coupling using the flux relations (40). We note that the most mobile species ethene displays an overshoot during equilibration. The dashed lines represent uptake simulations ignoring thermodynamic coupling and use uncoupled flux equation (54); in this scenario, no ethene overshoot is observed.

# 32. Transient overshoots for dehydrogenation of ethane using MFI catalyst

Hansen et al.<sup>83, 84</sup> describe the use of MFI catalyst for the dehydrogenation of ethane to produce ethene ethane(1) $\rightleftharpoons$  ethene(2)+hydrogen(3). In view of the low adsorption strength of hydrogen, the

reaction rate expressed as moles per kg catalyst per second may be written as

$$Rate = k_f q_1 - k_b q_2 \tag{66}$$

For our simulations we take  $k_f = 1 \text{ s}^{-1}$  and  $k_b = 1 \text{ s}^{-1}$ .

Figure 94 presents the simulation results for transient uptake inside MFI catalyst exposed to a gas phase ethane(1)/ethene(2)/hydrogen(3) mixture at 653 K. The partial pressures of the components in the bulk gas phase are  $p_1 = 0.2$  MPa;  $p_2 = 0.1$  MPa,  $p_3 = 1$  MPa. Diffusional effects are quantified with  $D_{ethane}/r_c^2 = 2.5 \times 10^{-4} \text{ s}^{-1}$ ;  $D_{ethene}/r_c^2 = 5 \times 10^{-4} \text{ s}^{-1}$ ;  $D_{hydrogen}/r_c^2 = 1.25 \times 10^{-2} \text{ s}^{-1}$ . The continuous solid lines represent uptake simulations include thermodynamic coupling using the flux relations (40). We note that more mobile species hydrogen displays a slight overshoot during equilibration. The dashed lines represent uptake simulations ignoring thermodynamic coupling and use uncoupled flux equation (54); in this scenario, no hydrogen overshoot is observed.

# 33. Notation

A	surface area per kg of framework, m <sup>2</sup> kg <sup>-1</sup>
$b_{ m i}$	Langmuir constant for species $i$ , Pa <sup>-1</sup>
$b_{ m i}$	Langmuir-Freundlich constant, $Pa^{-\nu}$
Ci	molar concentration, mol m <sup>-3</sup>
$\overline{c}_i(t)$	spatial-averaged concentration of species $i$ inside particle, mol m <sup>-3</sup>
$c_{t}$	total pore concentration in mixture, mol m <sup>-3</sup>
$d_{ m p}$	pore diameter, m
$D_{\rm i}$	Maxwell-Stefan diffusivity for molecule-wall interaction, m <sup>2</sup> s <sup>-1</sup>
$D_{ m ij}$	M-S exchange coefficient for <i>n</i> -component mixture, $m^2 s^{-1}$
$D^{ heta}_{ij}$	M-S exchange coefficient for <i>n</i> -component mixture defined by equation (23), $m^2 s^{-1}$
$D_{12}$	M-S exchange coefficient for binary mixture, m <sup>2</sup> s <sup>-1</sup>
[D]	matrix of diffusivities, m <sup>2</sup> s <sup>-1</sup>
$f_{ m i}$	partial fugacity of species <i>i</i> , Pa
n	number of species in the mixture, dimensionless
$k_1$	forward reaction rate constant, s <sup>-1</sup>
$k_2$	backward reaction rate constant, s <sup>-1</sup>
L	length of packed bed adsorber, m
$M_{ m i}$	molar mass of species $i$ , kg mol <sup>-1</sup>
М	excess amount injected in Taylor dispersion experiment, mol
$N_{ m i}$	molar flux of species <i>i</i> with respect to framework, mol $m^{-2} s^{-1}$
$p_{ m i}$	partial pressure of species <i>i</i> in mixture, Pa
$p_{\mathrm{t}}$	total system pressure, Pa
$q_{ m i}$	component molar loading of species $i$ , mol kg <sup>-1</sup>
$q_{ m i,sat}$	molar loading of species <i>i</i> at saturation, mol $kg^{-1}$
$q_{\mathrm{t}}$	total molar loading in mixture, mol kg <sup>-1</sup>
$\overline{q}_i(t)$	spatial-averaged component uptake of species $i$ , mol kg <sup>-1</sup>

r	radial direction coordinate, m
r <sub>c</sub>	radius of crystallite, m
R	gas constant, 8.314 J mol <sup>-1</sup> K <sup>-1</sup>
Sperm	membrane permeation selectivity, dimensionless
t	time, s
Т	absolute temperature, K
и	cross-sectional averaged velocity in tube, m s <sup>-1</sup>
ui	velocity of motion of adsorbate species $i$ with respect to the framework material, m s <sup>-1</sup>
ν	interstitial gas velocity in packed bed, m s <sup>-1</sup>
$V_{\rm p}$	pore volume, m <sup>3</sup> kg <sup>-1</sup>
x <sub>i</sub>	mole fraction of species <i>i</i> in adsorbed phase, dimensionless
Ζ	distance coordinate, m

#### Greek letters

$$\beta \qquad \text{dimensionless parameter, } \beta \equiv \sqrt{\frac{\frac{D_2(0)}{D_1(0)} \left(\Lambda \frac{k_1}{k_2} + 1\right)}{\Lambda \left(\frac{D_2(0)}{D_1(0)} \frac{k_1}{k_2} + 1\right)}}$$

γ	confinement parameter, $\gamma = 0$ for weak , $\gamma = 1$ for strong, dimensionless
δ	thickness of microporous membrane, m
${\delta}_{ m ij}$	Kronecker delta, dimensionless
ε	fractional pore volume of particle, dimensionless
ε	voidage of packed bed, dimensionless
$\phi$	Thiele modulus, $\phi \equiv \frac{r_c}{3} \sqrt{\frac{k_1}{D_1(0)} + \frac{k_2}{D_2(0)}}$ , dimensionless
Φ	modified Thiele modulus; see Table 1 of by Baur and Krishna <sup>21</sup> , dimensionless
$\Gamma_{ij}$	thermodynamic factors, dimensionless
[Γ]	matrix of thermodynamic factors, dimensionless

effectiveness factor, dimensionless

$$\Lambda \qquad \text{dimensionless diffusivity ratio, } \Lambda \equiv \frac{D_2(0)}{D_1(0)} \frac{\left(1 + (\theta_{1s} + \theta_{2s}) \frac{D_1(0)}{D_{12}(0)}\right)}{\left(1 + (\theta_{1s} + \theta_{2s}) \frac{D_2(0)}{D_{12}(0)}\right)}$$

$\mu_{\rm i}$	molar chemical potential of component <i>i</i> , J mol <sup>-1</sup>	
1		

 $\mu_i^0$  molar chemical potential of component *i* at standard state, J mol<sup>-1</sup>

- $v_i$  reaction stoichiometric coefficient, dimensionless
- v Freundlich exponent, dimensionless
- $\pi$  spreading pressure, N m<sup>-1</sup>
- $\theta_{i}$  fractional occupancy of component *i*, dimensionless
- $\theta_{\rm V}$  fractional vacancy,  $\theta_{\rm V} = 1 \theta_1 \theta_2$ , dimensionless

 $\theta_{is}$  fractional occupancy at catalyst surface, dimensionless

 $\theta_{i0}$  fractional occupancy at centre of catalyst, dimensionless

$$\Theta$$
 dimensionless parameter,  $\Theta = \frac{\sqrt{2(1 - 1/\Psi^2 - 2\ln(\Psi)/\Psi^2)}}{|1 - 1/\Psi^2|}$ 

$$\Xi \equiv \sqrt{\frac{1}{\theta_{Vs}^{\gamma}} \left(1 + \left(\theta_{1s} + \theta_{2s}\right) \frac{D_1(0)}{D_{12}(0)}\right)}$$

$$\Psi \qquad \text{dimensionless parameter, } \Psi \equiv \sqrt{\frac{\left(\Lambda + (1 - \Lambda)\theta_{1s}\right)k_1 + \left(1 + (\Lambda - 1)\theta_{2s}\right)k_2}{\left(\Lambda k_1 + k_2\right)}}$$

 $\rho$  framework density, kg m<sup>-3</sup>

au tortuosity, dimensionless

au time, dimensionless

#### **Subscripts**

- i referring to component *i*
- t referring to total mixture
- 0 referring to surface at centre of catalyst,  $\xi = 0$ .

1	referring to species 1
2	referring to species 2
S	referring to surface at position $\xi = 1$ .
sat	referring to saturation conditions
V	vacancy
ξ	at position $\xi$ within catalyst

Table 1. Dual-Langmuir parameter fits for  $CO_2$  and  $H_2$  in MFI (silicalite-1) zeolite. The  $CO_2$  isotherm fits are based on CBMC simulation data at three different temperatures, 200 K, 253 K, and 300 K. The  $H_2$  fits are based on CBMC simulation data at 300 K, combined with experimental data of Golden and Sircar <sup>85</sup> at 305.15 K, and 353.25 K.

$$\Theta = \Theta_{A,sat} \frac{b_A p}{1 + b_A p} + \Theta_{B,sat} \frac{b_B p}{1 + b_B p}; \ b_A = b_{A0} \exp\left(\frac{E_A}{RT}\right); \ b_B = b_{B0} \exp\left(\frac{E_B}{RT}\right)$$

	Site A			Site B		
	$\Theta_{i,A,sat}$	$b_{ m i,A}$	E <sub>A</sub>	$\Theta_{i,B,sat}$	$b_{\mathrm{i,B}}$	EB
	molecules uc <sup>-1</sup>	$Pa^{-1}$	kJ mol <sup>-1</sup>	molecules uc <sup>-1</sup>	Pa <sup>-1</sup>	kJ mol <sup>-1</sup>
CO <sub>2</sub>	21	1.56×10 <sup>-10</sup>	26	6.2	1.9×10 <sup>-14</sup>	31
H <sub>2</sub>	32	5.8×10 <sup>-10</sup>	10	41	2.18×10 <sup>-11</sup>	10



Table 2. 1-site Langmuir parameters for  $CO_2$  and  $C_2H_6$  in DDR zeolite at 298 K. These parameters have been fitted from the data scanned from Figure 36, Chapter 4 of the PhD dissertation of Binder.<sup>41</sup>



 $\begin{tabular}{|c|c|c|c|c|c|c|} \hline $q_{sat}$ & $b$ \\ $mol kg^{-1}$ & $Pa^{-1}$ \\ \hline $Pa^{-1}$ \\ \hline $CO_2$ & $2.8$ & $1.04 \times 10^{-5}$ \\ \hline $C_2H_6$ & $1.8$ & $6.6 \times 10^{-5}$ \\ \hline \end{tabular}$ 

Table 3. 1-site Langmuir parameters for  $N_2$  and  $CH_4$  in LTA-4A zeolite at 194 K. These parameters have been fitted from the isotherm data scanned from the paper by Habgood<sup>42</sup>

	$q_{ m sat}$	b
	mol kg <sup>-1</sup>	$Pa^{-1}$
N <sub>2</sub>	3.6	9.4×10 <sup>-5</sup>
CH <sub>4</sub>	3.6	2.08×10 <sup>-4</sup>

Table 4. 1-site Langmuir parameters for  $O_2$  and  $N_2$  Carbon Molecular Sieve (CMS).

	$q_{ m sat}$	b
	mol kg <sup>-1</sup>	$Pa^{-1}$
O <sub>2</sub>	1.9	1.45×10 <sup>-6</sup>
N <sub>2</sub>	1.4	1.5×10 <sup>-6</sup>

Table 5. Dual-site Langmuir-Freundlich parameters for pure component isotherms for hexane and butane isomers in MFI at 298 K. This data is from the Supporting Information of Titze et al.<sup>45</sup> The unary isotherm data are fitted with the dual-Langmuir-Freundlich model

$$\Theta_{i} = \Theta_{i,A,sat} \frac{b_{i,A} p_{i}^{\nu_{A}}}{1 + b_{i,A_{i}}^{\nu_{A}}} + \Theta_{i,B,sat} \frac{b_{i,B} p_{i}^{\nu_{B}}}{1 + b_{i,B} p_{i}^{\nu_{B}}}$$



Bulk fluid phase fugacity,  $f_i$  / Pa

Bulk fluid phase fugacity,  $f_i$  / Pa

	Site A			Site B		
	$\Theta_{i,A,sat}$	$b_{ m i,A}$	V <sub>i,A</sub>	$\Theta_{i,B,sat}$	$b_{\mathrm{i,B}}$	$V_{i,B}$
	molecules uc <sup>-1</sup>	$\mathrm{Pa}^{-\nu_i}$	dimensionless	molecules uc <sup>-1</sup>	$\mathrm{Pa}^{-\nu_i}$	dimensionless
nC6	6.6	0.708	0.83	1.4	16.6	1.5
2MP	4	4.51	1.05	4	7.92×10 <sup>-6</sup>	1.13
nC <sub>4</sub> H <sub>10</sub>	1.5	2.24×10 <sup>-3</sup>	0.57	8.7	9.75×10 <sup>-3</sup>	1.12
iC <sub>4</sub> H <sub>10</sub>	4	2.29×10 <sup>-2</sup>	1	6	2.87×10 <sup>-5</sup>	1

Table 6. Single-site Langmuir parameters, and M-S diffusivities  $D_i/r_c^2$ , for pure component 2MB, 2MP, and 22DMB at 473 K in MFI zeolite. The parameters are based on the experimental data of Jolimaître et al.<sup>59, 60</sup> All simulations of the breakthrough experiments of Jolimaître et al.<sup>59</sup> were performed for extrudate 2; bed voidage,  $\varepsilon = 0.4$ ; density of extrudate 2,  $\rho = 620.8$  kg m<sup>-3</sup>; The interstitial velocity *v* varied with each run and were taken from Table 6 of Jolimaître et al.<sup>59</sup> The partial pressures of each of the components 2MB, 2MP, and 22DMB at the inlet to the adsorber are specified using the data provided in Table 6 of Jolimaître et al.<sup>59</sup>

$$\Theta_i^0(p) = \frac{\Theta_{i,sat}b_ip}{1+b_ip}$$

	$\Theta_{i,sat}$ molecules uc <sup>-1</sup>	b <sub>i</sub> Pa <sup>-1</sup>	$D_i/r_c^2$ s <sup>-1</sup>
2MB	4	4.12×10 <sup>-5</sup>	0.0075
2MP	4	1.27×10 <sup>-4</sup>	0.005
22DMB	4	7.12×10 <sup>-5</sup>	0.0000625

Table 7. 1-site Langmuir parameters for propene and propane in ZIF-8.<sup>86</sup> The *T*-dependent parameters are obtained by fitting the combined sets of pure component isotherm data of Li et al.<sup>57</sup> and Böhme et al.<sup>87</sup> determined for a variety of temperatures in the range 273 K to 408 K.



Table 8. Dual-site Langmuir-Freundlich parameters for pure component isotherms in MFI at 300 K. Note that the saturation capacities are specified in molecules per unit cell; multiply these by 0.1734 to obtain the loading values in mol per kg framework. The fits are based on CBMC simulation data from a variety of previous works.<sup>5, 10, 12-16, 20, 25, 27, 50, 88-91</sup> The unary isotherm data are fitted with the dual-

Langmuir-Freundlich model  $\Theta_i = \Theta_{i,A,sat} \frac{b_{i,A} p_i^{\nu_A}}{1 + b_{i,A_i}^{\nu_A}} + \Theta_{i,B,sat} \frac{b_{i,B} p_i^{\nu_B}}{1 + b_{i,B} p_i^{\nu_B}}$ 



Bulk fluid phase fugacity, f<sub>i</sub>/Pa

	Site A			Site B		
	$\Theta_{i,A,sat}$	$b_{\mathrm{i,A}}$	$\mathcal{V}_{i,A}$	$\Theta_{i,B,sat}$	$b_{\mathrm{i,B}}$	$ u_{i,B}$
	molecules uc <sup>-1</sup>	$\mathrm{Pa}^{-\nu_i}$	dimensionless	molecules uc <sup>-1</sup>	$\mathrm{Pa}^{-\nu_i}$	dimensionless
CO <sub>2</sub>	19	6.12×10 <sup>-6</sup>	1	11	1.73×10 <sup>-8</sup>	1
H <sub>2</sub>	30	3.57×10 <sup>-8</sup>	1	42	1.39×10 <sup>-9</sup>	1
CH <sub>4</sub>	16	3.1×10 <sup>-6</sup>	1	7	5×10 <sup>-9</sup>	1
$nC_4H_{10}$	1.5	2.24×10 <sup>-3</sup>	0.57	8.7	9.75×10 <sup>-3</sup>	1.12

Table 9. Dual-site Langmuir-Freundlich parameters for pure component 1-alcohols in CHA at 300 K. The fit parameters are based on the CBMC simulations of pure component isotherms presented in earlier work.<sup>62</sup> Note that the saturation capacities are specified in molecules per cage; multiply these by 1.387 to obtain the values in mol per kg framework.



Bulk fluid phase fugacity,  $f_i$  / Pa

	Site A			Site B		
	$\Theta_{i,A,sat}$	$b_{ m i,A}$	$\mathcal{V}_{i,A}$	$\Theta_{i,B,sat}$	$b_{ m i,B}$	$\mathcal{V}_{i,B}$
	Molecules cage <sup>-1</sup>	$\mathrm{Pa}^{-\nu_i}$	dimensionless	molecules cage <sup>-1</sup>	$Pa^{-\nu_i}$	dimensionless
methanol	2.7	6.77×10 <sup>-11</sup>	3.3	2.7	4.45×10 <sup>-4</sup>	1
ethanol	2	7.93×10 <sup>-5</sup>	0.87	2	3.6×10 <sup>-3</sup>	1.14
1-propanol	1	1.28×10 <sup>-2</sup>	1.8	1	9.11×10 <sup>-2</sup>	1
1-butanol	1	0.231	1.46	1	0.5066	1
1-pentanol	0.5	19.26	1.72	0.5	6.91	1
1-hexanol	0.5	2561	2.4	0.5	24.8	1

Table 10. Single-site Langmuir fit parameters of the isotherms for m-xylene and p-xylene in MFI zeolite at 300 K. The pure component isotherms are obtained from the molecular simulation data (for the orthorhombic (often denoted as ORTHO) MFI framework) of Chempath et al.<sup>71</sup> The p-xylene data is considered to reach saturation at 4 molecules per unit cell.

$$\Theta_i^0(p) = \frac{\Theta_{i,sat}b_ip}{1+b_{i,p}}$$

	$\Theta_{i,sat}$	$b_{ m i}$
	molecules uc <sup>-1</sup>	Pa <sup>-1</sup>
m-xylene	4	1.2
p-xylene	4	0.6

Table 11. Dual-site Langmuir-Freundlich parameters for pure component water, methanol, and ethanol at 300 K in all-silica DDR zeolite. The fit parameters are based on the CBMC simulations of pure component isotherms presented in earlier work.<sup>92</sup> Note that the saturation capacities are specified in molecules per cage; multiply these by 0.832157 to obtain the values in mol per kg framework.



$$\Theta_i^0(p) \equiv \Theta_{i,A} + \Theta_{i,B} = \frac{\Theta_{i,sat,A}b_{i,A}p}{1 + b_{i,A}p} + \frac{\Theta_{i,sat,B}b_{i,B}p}{1 + b_{i,B}p}$$

	Site A			Site B		
	$\Theta_{i,A,sat}$	$b_{ m i,A}$	$\mathcal{V}_{i,A}$	$\Theta_{i,B,sat}$	$b_{\mathrm{i,B}}$	$V_{i,B}$
	Molecules cage <sup>-1</sup>	$Pa^{-\nu_i}$	dimensionless	molecules cage <sup>-1</sup>	$Pa^{-\nu_i}$	dimensionless
water	8.083	3.85×10 <sup>-16</sup>	4	2.667	1.73×10 <sup>-5</sup>	1
methanol	2.1667	1.49×10 <sup>-4</sup>	1.25	1.9167	6×10 <sup>-4</sup>	0.77
ethanol	1.8167	7.66×10 <sup>-3</sup>	1	0.775	8.59×10 <sup>-6</sup>	1

Table 12. Dual-Langmuir-Freundlich fits of the isotherms of water, and ethanol in LTA-4A zeolite. The isotherm fits are based on the experimental data of Pera-Titus et al.<sup>77</sup>



Bulk gas phase pressure,  $p_i$  /Pa

Bulk gas phase pressure, *p*<sub>i</sub> /Pa

	Site A			Site B				
	$q_{\mathrm{A,sat}}$	$b_{ m A0}$	E <sub>A</sub>	VA	$q_{ m B,sat}$	$b_{ m B0}$	EB	VB
	mol kg <sup>-1</sup>	$\mathrm{Pa}^{-\nu_i}$	kJ mol <sup>-1</sup>	dimensionless	mol kg <sup>-1</sup>	$\mathrm{Pa}^{-\nu_i}$	kJ mol <sup>-1</sup>	dimensionless
water	2.1	2.1×10 <sup>-60</sup>	269	7.26	9.7	5.81×10 <sup>-8</sup>	33	0.83
ethanol	1.85	5.24×10 <sup>-13</sup>	43.3	1.9	1.4	2.65×10 <sup>-10</sup>	40	1.7

Table 13. Calculation of modified Thiele modulus for various scenarios. Adapted from Baur and Krishna.<sup>21</sup>

Scenario	Formula for modified Thiele Modulus	Remarks about analytic solution
Equal diffusivities: $D_1(0) = D_2(0)$	$\Phi = \phi \Xi$	Exact for facile exchange. For finite exchange, a very good approximation.
Strong confinement	$\Phi = \phi \ \beta \ \Xi \Psi$	Exact for facile exchange. For finite exchange, a very good approximation.
Weak confinement	$\Phi = \frac{\phi \beta \Xi \Psi}{\Theta}$	Exact for facile exchange in the limiting cases $\phi \rightarrow \infty$ and $\phi \rightarrow 0$ . For all other cases, including that for finite exchange, a very good approximation.

(1) Classical scenario:  $\Phi = \phi$ .

(2) Weak confinement scenario for the diffusivities. Also ignored are the correlation effects, i.e.  $D_1/D_{12} \rightarrow 0$ ;  $D_2/D_{12} \rightarrow 0$ . Thermodynamic coupling effects are accounted for using the mixed-gas Langmuir

isotherm model.  $\Phi = \frac{\phi \ \beta \Xi \Psi}{\Theta}$ 

- (3) Strong confinement scenario for the diffusivities in which the diffusivities are related to the zero-loading diffusivities by  $D_i = D_i(0)\theta_V$ . Also ignored are the correlation effects, i.e.  $D_1/D_{12} \rightarrow 0$ ;  $D_2/D_{12} \rightarrow 0$ . Thermodynamic coupling effects are accounted for using the mixed-gas Langmuir isotherm model.  $\Phi = \phi \beta \Xi \Psi$
- (4) Weak confinement scenario for the diffusivities. Thermodynamic coupling effects are accounted for using the mixedgas Langmuir isotherm model. Correlation effects are accounted for with finite values of  $D_1/D_{12}$ ;  $D_2/D_{12}$ .

$$\Phi = \frac{\phi \ \beta \Xi \Psi}{\Theta}$$

(5) Strong confinement scenario for the diffusivities in which the diffusivities are related to the zero-loading diffusivities by  $D_i = D_i(0)\theta_V$ . Thermodynamic coupling effects are accounted for using the mixed-gas Langmuir isotherm model. Correlation effects are accounted for with finite values of  $D_1/D_{12}$ ;  $D_2/D_{12}$ .  $\Phi = \phi \beta \Xi \Psi$  Table 14. Dual-site Langmuir parameters for hexane isomers in MFI at 362 K. The fits correspond to CBMC simulations. <sup>17, 93, 94</sup>

$$\Theta_i^0(p) \equiv \Theta_{i,A} + \Theta_{i,B} = \frac{\Theta_{i,sat,A}b_{i,A}p}{1 + b_{i,A}p} + \frac{\Theta_{i,sat,B}b_{i,B}p}{1 + b_{i,B}p}$$

Component	Dual Langmuir Parameters				
-	6				
	Site A		Site B		
	$b_{ m i,A}$	$\Theta_{i,sat,A}$	$b_{\mathrm{i,B}}$	$\Theta_{i,sat,B}$	
	/Pa <sup>-1</sup>	/molecules uc <sup>-1</sup>	/Pa <sup>-1</sup>	/molecules uc <sup>-1</sup>	
nC <sub>6</sub>	6.32 ×10 <sup>-2</sup>	4.0	1.7 ×10 <sup>-3</sup>	4.0	
3MP	4.75 ×10 <sup>-2</sup>	4.0	2.27 ×10 <sup>-5</sup>	2.3	
2DMB	$1.085 \times 10^{-2}$	4.0	2.27 ×10 <sup>-5</sup>	0.0	

Table 15. Single-site Langmuir fit parameters of the isotherms for hydrogen, ethene, ethane, benzene, and ethylbenzene in MFI zeolite at 653 K. The pure component isotherms are obtained from the molecular simulation data of Hansen et al.<sup>83, 84</sup> for the range of pressure up to 1 MPa. Hansen provides the isotherm fit parameters for a 3-site Langmuir fit. For our purposes in this article the simpler single

site  $\Theta_i^0(p) = \frac{\Theta_{i,sat}b_ip}{1+b_{i,p}}$  is of sufficient accuracy for total mixture loadings below 4 molecules per unit

cell.

	$\Theta_{i,sat}$	b <sub>i</sub>
	molecules uc <sup>-1</sup>	$\mathbf{Pa}^{-1}$
hydrogen	4	5 ×10 <sup>-8</sup>
ethene	4	$2.75 \times 10^{-7}$
ethane	4	6 ×10 <sup>-7</sup>
benzene	4	1.93 ×10 <sup>-6</sup>
ethylbenzene	4	$2.55 \times 10^{-6}$

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#### **35.** Caption for Figures

Figure 1. (a) MD data on the M-S diffusivities of various guest molecules in (a) all-silica FAU zeolite, (b) MFI zeolite, and (c) IRMOF-1. The MD data are at 300 K. The *x*-axis is the spreading pressure calculated on the basis of the molar loadings used in the MD simulations, in conjunction with CBMC simulation data for the unary isotherms of the guest molecules. (b) MD data on the M-S diffusivities of CH<sub>4</sub> in various host materials. The MD data are at 300 K. The *x*-axis is the spreading pressure calculated on the basis of the molar loadings used in the MD simulations, in conjunction with CBMC simulation data for the unary isotherms of the guest molecules.

Figure 2. Experimental data on the M-S diffusivity,  $D_i$ , of is-butane in MFI as a function of the spreading pressure,<sup>95</sup> compared with the corresponding dependence of the inverse thermodynamic factor  $1/\Gamma_i$ .

Figure 3. Dependence of the Maxwell-Stefan diffusivity  $D_i$ , and the inverse thermodynamic factor  $1/\Gamma_i$ in CuBTC of (a) n-butane, (b) iso-butane, (c) 2,2-dimethylpropane, and (d) 2-methylbutane on the spreading pressure. These data are re-plotted using the information from the published literature.<sup>11</sup>

Figure 4. The M-S binary exchange coefficients  $D_{12}$ , for diffusion of equimolar ( $c_1 = c_2$ ) binary mixtures (a) H<sub>2</sub>/CH<sub>4</sub>, (b) CH<sub>4</sub>/Ar, (c) CH<sub>4</sub>/C<sub>2</sub>H<sub>6</sub>, (d) CO<sub>2</sub>/ CH<sub>4</sub>, (e) CO<sub>2</sub>/H<sub>2</sub>, and (f) CO<sub>2</sub>/N<sub>2</sub> at 300 K in a variety of host materials as a function of the total pore concentration,  $c_t = (q_1 + q_2)/V_p$ . The  $D_{12,fl}$  for binary *fluid phase* mixture diffusion, obtained from independent MD simulations. The MD data are culled from the published literature.<sup>5, 13, 15, 20, 26, 27, 50, 88, 96-99</sup>.

Figure 5. MD simulation data for the degree of correlations,  $D_1/D_{12}$ , for diffusion of equimolar binary mixtures ( $c_1 = c_2$ ) (a) H<sub>2</sub>/CO<sub>2</sub>, (b) CO<sub>2</sub>/CH<sub>4</sub>, (c) H<sub>2</sub>/CH<sub>4</sub>, (d) CH<sub>4</sub>/nC<sub>4</sub>H<sub>10</sub>, (e) CH<sub>4</sub>/C<sub>2</sub>H<sub>6</sub>, and (f) CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub> at 300 K in a variety of host materials, as a function of the total pore concentration,  $c_t = (q_1 + q_2)/V_p$ .

Figure 6. Discretization schemes for a single spherical crystallite.

Figure 7. Schematic of membrane permeation device.

Figure 8. MD simulation data for the degree of correlations,  $D_1/D_{12}$ , for diffusion of equimolar binary H<sub>2</sub>(1)/CH<sub>4</sub>(2), CH<sub>4</sub>(1)/nC<sub>4</sub>H<sub>10</sub>(2), CH<sub>4</sub>(1)/CO<sub>2</sub>(2), and H<sub>2</sub>(1)/CO<sub>2</sub>(2) mixtures in MFI zeolite at 300 K, as a function of the total mixture loading,  $q_t$ .

Figure 9. (a) Influence of  $D_1/D_{12}$  on the permeation selectivity,  $S_{\text{perm}}$ , of binary 95/5 CH<sub>4</sub>(1)/nC<sub>4</sub>H<sub>10</sub>(2) mixture permeation across MFI membrane at 300 K. The values of  $S_{\text{perm}}$  are calculated from steady-state permeation simulations for the fluxes and calculations using Equation (47), taking  $p_{1\delta} = p_{2\delta} \approx 0$  and  $p_{10}/p_{20} = 95/5$ . (b, c) The plots show the normalized fluxes  $N_1/(\rho q_{10} D_1/\delta)$ , and  $N_2/(\rho q_{20} D_2/\delta)$  as a function of the total upstream pressure. In the simulations the M-S diffusivity is assumed to be independent of the loading. The mixture adsorption equilibrium is calculated using IAST; the pure component isotherms are specified in Table 8.

Figure 10. (a, b) Experimental data of Sjöberg et al.<sup>35</sup> for steady-state permeation of 50/50 equimolar H<sub>2</sub>(1)/CO<sub>2</sub>(2) mixtures across MFI (silicalite-1) zeolite membrane at 273 K. The continuous solid lines are the steady-state permeation flux calculations using the following diffusivity:  $\rho D_1 / \delta = 64$  kg m<sup>-2</sup> s<sup>-1</sup>,  $\rho D_2 / \delta = 3.2$  kg m<sup>-2</sup> s<sup>-1</sup>; and  $D_1 / D_{12} = 20$ . The downstream compartment pressure = 1 bar, with partial pressures,  $p_{1\delta} = 95$  kPa;  $p_{2\delta} = 5$  kPa; these estimates are based on the data on separation factors determined experimentally. The mixture adsorption equilibrium is calculated using IAST; the unary isotherm data is provided in Table 1. The model used for the flux calculations correspond to Equations (3), and (4) of our earlier work;<sup>25</sup> these equations are based on the model in which the loading dependence of the M-S diffusivities are taken to be proportional to the vacancy:  $D_i(\theta) = D_i(0)\theta_i$ ; for this assumption the [ $\Gamma$ ] "drops out" in the final expressions because they "cancel out" with the vacancy corrections, as explained in the Supporting Information to our work. (b) For H<sub>2</sub>(1) flux, the experimental data of Sjöberg are also compared to the model neglecting correlations, Equation (40), and the dominant correlations model, Equation (48).

Figure 11. Schematic of fixed bed adsorber.

Figure 12. Pore landscape and structural details of DDR zeolite.<sup>5, 37</sup>

Figure 13. Pore landscape and structural details of DDR zeolite.<sup>5, 37</sup>

Figure 14. Window dimensions, and structural details of DDR zeolite.

Figure 15. Molecular dimensions of  $CO_2$  and  $C_2H_6$ .

Figure 16. Comparison of unary isotherm data with single-site Langmuir fits using the parameters reported in Table 2.

Figure 17. The symbols are scanned from Figure 3 of Binder et al;<sup>39</sup> they represent IAST calculations for binary CO<sub>2</sub> (1)/C<sub>2</sub>H<sub>6</sub>(2) mixture adsorption in DDR crystals with constant CO<sub>2</sub> partial pressures of  $p_1 = 20$ , 40, and 60 kPa for experiments 1, 2, and 3, respectively. The partial pressures of C<sub>2</sub>H<sub>6</sub> ethane in the gas phase is varied. The continuous solid lines are our calculations using mixed-gas Langmuir model using the single-site Langmuir parameters reported in in Table 2.

Figure 18. Elements of the matrix of thermodynamic correction factors  $\Gamma_{ij}$  as a function of total mixture loading,  $q_t$ , calculated using the mixed-gas Langmuir model for binary CO<sub>2</sub>(1)/C<sub>2</sub>H<sub>6</sub>(2) mixture adsorption in DDR for (a) 1:1, (b) 2:1, and (c) 3:1 ratios of partial pressures in the gas phase. In these calculations the total gas pressure,  $p_t$ , was varied from 1 to 100 kPa.

Figure 19. Calculations of  $(\Gamma_{12} q_2/\Gamma_{11} q_1)$ , and  $(\Gamma_{21} q_1/\Gamma_{22} q_2)$  as a function of total mixture loading,  $q_t$ , for binary CO<sub>2</sub>(1)/C<sub>2</sub>H<sub>6</sub>(2) mixture adsorption in DDR for 3:1 ratios of partial pressures in the gas phase. In these calculations the total gas pressure,  $p_t$ , was varied from 1 to 100 kPa.

Figure 20. The hexagonal crystals of DDR zeolite are modelled as spherical crystals of radius  $r_c$ . The single spherical crystallite of DDR zeolite is divided into 100 equidistant segments in the numerical procedure for determining transient uptakes.

Figure 21. The dependence of the diffusivities  $D_1/r_c^2$ , and  $D_2/r_c^2$  for CO<sub>2</sub>(1), and C<sub>2</sub>H<sub>6</sub>(2) in DDR on the corresponding component loadings,  $q_1$ , and  $q_2$ , in the adsorbed phase at equilibrium.

Figure 22. Experimental data of Binder<sup>39</sup> for transient uptake of 1:1 CO<sub>2</sub>(1)/C<sub>2</sub>H<sub>6</sub>(2) within crystals of DDR zeolite. In the bulk gas phase 298 K,  $p_1 = 20$  kPa,  $p_2 = 20$  kPa. The parameter values are  $D_1/r_c^2 = 0.125$  s<sup>-1</sup>;  $D_1/D_2 = 1333$ . The continuous solid lines are the calculations using Equation (40). The dashed lines are the calculations using uncoupled flux equation (54).

Figure 23. Experimental data of Binder<sup>39</sup> for transient uptake of 2:1 CO<sub>2</sub>(1)/C<sub>2</sub>H<sub>6</sub>(2) within crystals of DDR zeolite. In the bulk gas phase 298 K,  $p_1 = 40$  kPa,  $p_2 = 20$  kPa. The parameter values are  $D_1/r_c^2 = 9.375 \times 10^{-3} \text{ s}^{-1}$ ;  $D_1/D_2 = 100$ . The continuous solid lines are the calculations using Equation (40). The dashed lines are the calculations using uncoupled flux equation (54).

Figure 24. Experimental data of Binder<sup>39</sup> for transient uptake of 3:1 CO<sub>2</sub>(1)/C<sub>2</sub>H<sub>6</sub>(2) within crystals of DDR zeolite. In the bulk gas phase 298 K,  $p_1 = 60$  kPa,  $p_2 = 20$  kPa. The parameter values are  $D_1/r_c^2 = 6.25 \times 10^{-3} \text{ s}^{-1}$ ;  $D_1/D_2 = 50$ . The continuous solid lines are the calculations using Equation (40). The dashed lines are the calculations using uncoupled flux equation (54).

Figure 25. Transient development of CO<sub>2</sub>(1), and C<sub>2</sub>H<sub>6</sub>(2) loadings along the radius of DDR crystal (center, r = 0; surface of crystal,  $r = r_c$ ) monitored at different times from start of the uptake. In the bulk gas phase 298 K,  $p_1 = 20$  kPa,  $p_2 = 20$  kPa. The input data are the same as in Figure 22.

Figure 26. Transient development of CO<sub>2</sub>(1), and C<sub>2</sub>H<sub>6</sub>(2) loadings along the radius of DDR crystal (center, r = 0; surface of crystal,  $r = r_c$ ) monitored at different times from start of the uptake.

Figure 27. Transient development of  $CO_2(1)$ , and  $C_2H_6(2)$  loadings along the radius of DDR crystal (center, r = 0; surface of crystal,  $r = r_c$ ) monitored at different times from start of the uptake. In the bulk gas phase 298 K,  $p_1 = 60$  kPa,  $p_2 = 20$  kPa. The input data are the same as in Figure 24.

Figure 28. Transient development of "corrected" loadings  $q_1(\mu_1 - \mu_1^0)/RT = \Gamma_{11}q_1 + \Gamma_{12}q_2$ , and  $q_2(\mu_2 - \mu_2^0)/RT = \Gamma_{21}q_1 + \Gamma_{22}q_2$  of CO<sub>2</sub>(1), and C<sub>2</sub>H<sub>6</sub>(2) along the radius of DDR crystal (center, r = 0; surface of crystal,  $r = r_c$ ) monitored at different times from start of the uptake. In the bulk gas phase 298 K,  $p_1 = 40$  kPa,  $p_2 = 20$  kPa. The input data are the same as in Figure 23.

Figure 29. Transient development of "corrected" loadings  $q_1(\mu_1 - \mu_1^0)/RT = \Gamma_{11}q_1 + \Gamma_{12}q_2$ , and  $q_2(\mu_2 - \mu_2^0)/RT = \Gamma_{21}q_1 + \Gamma_{22}q_2$  of CO<sub>2</sub>(1), and C<sub>2</sub>H<sub>6</sub>(2) along the radius of DDR crystal (center, r = 0; surface of crystal,  $r = r_c$ ) monitored at different times from start of the uptake. In the bulk gas phase 298 K,  $p_1 = 60$  kPa,  $p_2 = 20$  kPa. The input data are the same as in Figure 24.

Figure 30. Transient development of the chemical potentials  $(\mu_1 - \mu_1^0)/RT$ , and  $(\mu_2 - \mu_2^0)/RT$  along the radius of DDR crystal (center, r = 0; surface of crystal,  $r = r_c$ ) of CO<sub>2</sub>(1), and C<sub>2</sub>H<sub>6</sub>(2) monitored at different times from start of the uptake. In the bulk gas phase 298 K,  $p_1 = 60$  kPa,  $p_2 = 20$  kPa. The input data are the same as in Figure 24.

Figure 31. Experimental data of Binder<sup>39</sup> for transient development of molar loadings of CO<sub>2</sub>(1), and C<sub>2</sub>H<sub>6</sub>(2) along the radius of DDR crystal monitored at different times from start of the uptake. In the bulk gas phase 298 K,  $p_1 = 40$  kPa,  $p_2 = 20$  kPa. The experimental data in (a) has been scanned from Figure S1 of the Supporting Information accompanying the paper by Binder.<sup>39</sup>

Figure 32. Experimental data of Binder<sup>39</sup> for transient development of "corrected" molar loadings  $q_1(\mu_1 - \mu_1^0)/RT = \Gamma_{11}q_1 + \Gamma_{12}q_2$ , and  $q_2(\mu_2 - \mu_2^0)/RT = \Gamma_{21}q_1 + \Gamma_{22}q_2$  of CO<sub>2</sub>(1), and C<sub>2</sub>H<sub>6</sub>(2) along the radius of DDR crystal monitored at different times from start of the uptake. In the bulk gas phase 298 K,  $p_1 = 40$  kPa,  $p_2 = 20$  kPa.

Figure 33. Transient breakthrough of 10/90 CO<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> mixtures through fixed bed adsorber packed with DDR crystals operating at 298 K, and total pressure  $p_t = 100$  kPa. The parameter values are: L = 0.3 m; voidage of bed,  $\varepsilon = 0.4$ ; interstitial gas velocity, v = 0.1 m/s; radius of crystallite,  $r_c = 40 \ \mu\text{m}$ ;  $D_1/r_c^2 = 0.00125 \ \text{s}^{-1}$ ;  $D_1/D_2 = 1333$ .

Figure 34. Structural details for LTA-4A zeolite.<sup>29</sup>

Figure 35. Experimental data of Habgood<sup>42</sup> on transient uptake of N<sub>2</sub>(1)/CH<sub>4</sub>(2) mixture within LTA-4A crystals, exposed to binary gas mixtures at 194 K and partial pressures  $p_1 = 50.9$  kPa;  $p_2 = 49.1$  kPa. Maxwell-Stefan diffusivities:  $D_1/r_c^2 = 1.56 \times 10^{-5}$  s<sup>-1</sup>;  $D_2/r_c^2 = 7.2 \times 10^{-9}$  s<sup>-1</sup>. The continuous solid lines

are the calculations using Equation (40). The dashed lines are the calculations using uncoupled flux equation (54). Table 3 provides the 1-site Langmuir parameters for  $N_2$  and  $CH_4$  in LTA-4A zeolite at 194 K.

Figure 36. Transient development of N<sub>2</sub>(1), and CH<sub>4</sub>(2) loadings along the radius of LTA-4A crystal (center, r = 0; surface of crystal,  $r = r_c$ ) monitored at different times from start of the uptake. The input data are the same as in Figure 35.

Figure 37. Transient development of "corrected" loadings  $q_1(\mu_1 - \mu_1^0)/RT = \Gamma_{11}q_1 + \Gamma_{12}q_2$ , and  $q_2(\mu_2 - \mu_2^0)/RT = \Gamma_{21}q_1 + \Gamma_{22}q_2$  of N<sub>2</sub>(1), and CH<sub>4</sub>(2) along the radius of LTA-4A crystal (center, r = 0; surface of crystal,  $r = r_c$ ) monitored at different times from start of the uptake. The input data are the same as in Figure 35.

Figure 38. Experimental data of Chen et al.<sup>44</sup> for transient uptake of O<sub>2</sub>(1)/N<sub>2</sub>(2) mixture in carbon molecular sieve (CMS) at 300 K exposed to binary gas mixtures at partial pressures  $p_1 = 109.6$  kPa;  $p_2 =$ 432.56 kPa. The continuous solid lines are transient uptake simulations use Equation (40) taking  $D_{O2}/r_c^2 = 3.5 \times 10^{-4} \text{ s}^{-1}$ ;  $D_{N2}/r_c^2 = 9.5 \times 10^{-6} \text{ s}^{-1}$ ;  $D_{O2}/D_{N2} = 36.8$ . The dashed lines are the calculations using uncoupled flux equation (54). The unary isotherm data are provided in Table 4.

Figure 39. Transient development of  $O_2(1)$ , and  $N_2(2)$  loadings along the radius of CMS particle (center, r = 0; surface of particles,  $r = r_c$ ) monitored at different times from start of the uptake. The input data are the same as in Figure 38.

Figure 40. Pore landscape for MFI zeolite.

Figure 41. Structural details for MFI zeolite.

Figure 42. Experimental data of Titze et al.<sup>45</sup> for Run 1 transient uptake of nC6/2MP mixtures in MFI zeolite. The continuous solid lines are Maxwell-Stefan model simulation results using Equation (40) that includes thermodynamic coupling. The dashed lines are the calculations using uncoupled flux equation (54). Input data simulation of Run 1:  $D_1/r_c^2 = 0.016 \text{ s}^{-1}$ ;  $D_2/r_c^2 = 1.6 \times 10^{-4} \text{ s}^{-1}$ ; t = 0;  $p_1(r_c, 0) = p_2(r_c, 0) = 0$  Pa;  $t \ge 0$ ;  $p_1(r_c, t) = p_2(r_c, t) = 1.3$  Pa. The isotherm data are provided in Table 5. The mixture adsorption equilibrium is determined using the IAST.

Figure 43. Transient development of nC6, and 2MP loadings along the radius of MFI crystal (center, r = 0; surface of crystal,  $r = r_c$ ) monitored at different times from start of the uptake. The input data are the same as in Figure 42.

Figure 44. Transient development of "corrected" loadings  $q_1(\mu_1 - \mu_1^0)/RT = \Gamma_{11}q_1 + \Gamma_{12}q_2$ , and  $q_2(\mu_2 - \mu_2^0)/RT = \Gamma_{21}q_1 + \Gamma_{22}q_2$  of nC6, and 2MP along the radius of MFI crystal (center, r = 0; surface of crystal,  $r = r_c$ ) monitored at different times from start of the uptake. The input data are the same as in Figure 42.

Figure 45. Transient uptake of nC4/iC4 mixture in MFI at 298 K. The initial partial pressures  $p_1 = p_2 = 0$  Pa; final partial pressures  $p_1 = p_2 = 100$  Pa. Input data:  $D_1/r_c^2 = 0.08 \text{ s}^{-1}$ ;  $D_2/r_c^2 = 4 \times 10^{-3} \text{ s}^{-1}$ . The isotherm data are provided in Table 5. The mixture adsorption equilibrium is determined using the IAST. The continuous solid lines using Equation (40) that include thermodynamic coupling effects. The dashed lines are simulations using uncoupled flux equation (54).

Figure 46. Experimental data of Niessen and Karge<sup>47, 48</sup> for uptake of benzene(1)/ethylbenzene(2) mixture in MFI zeolite (H-ZSM-5). Also shown are transient uptake simulations taking the ratio of diffusivities  $D_1/D_2 = 100$ .

Figure 47. Experimental data of Niessen and Karge<sup>47, 48</sup> for uptake of benzene(1)/*p*-xylene(2) mixture in MFI zeolite (H-ZSM-5). Also shown are transient uptake simulations taking the ratio of diffusivities  $D_1/D_2 = 25$ .

Figure 48. Experimental data of Kärger and Bülow<sup>49</sup> for transient uptake of n-heptane(1)/benzene(2) mixture in NaX zeolite at 359 K. Input data:  $D_1/r_c^2 = 2 \times 10^{-4} \text{ s}^{-1}$ ;  $D_2/r_c^2 = 2 \times 10^{-6} \text{ s}^{-1}$ . The continuous solid lines using Equation (40) that include thermodynamic coupling effects. The dashed lines are simulations using uncoupled flux equation (54).

Figure 49. (a, b) Experimental data of Majumdar et al.<sup>53</sup> for transient uptake of (a) 10/90, and (b) 50/50 mixtures of  $N_2(1)/CH_4(2)$  mixtures in Ba-ETS-4 at 283 K and total pressure of 0.7 MPa. Note that the *y*-axes represent the fractional uptake of each component; this is obtained by dividing each of the component loadings by the final equilibrated loading within the crystal.

Figure 50. Transient uptake of (a) ethane/n-butane, (b) ethane/n-pentane, and (c) n-butane/n-pentane mixtures in extrudates of activated carbon (AC) at 303 K. Note that the *y*-axes correspond to the molar uptake normalized with respect to the final equilibrated molar loadings. The conditions are chosen to correspond to those in the experiments reported in Figures 8, 9, and 10 of Hu and Do.<sup>55</sup> The single-site Langmuir parameters are provided in Table 1 of Hu and Do.<sup>55</sup> The mixture adsorption equilibrium is determined using the IAST. The continuous solid lines using Equation (40) that include thermodynamic coupling effects. The dashed lines are simulations using uncoupled flux equation (54). Input data on diffusivities:  $D_{C2}/r_c^2 = 0.005 \text{ s}^{-1}$ ;  $D_{nC4}/r_c^2 = 9 \times 10^{-4} \text{ s}^{-1}$ ;  $D_{nC5}/r_c^2 = 3 \times 10^{-4} \text{ s}^{-1}$ .

Figure 51. The structure and pore landscapes of ZIF-8.

Figure 52. Structural details of ZIF-8.

Figure 53. Simulations of transient uptake of  $C_3H_6(1)/C_3H_8(2)$  within crystals of ZIF-8 at 303 K. The simulations use the isotherm parameters specified in Table 7, along with  $D_1/r_c^2 = 1.5 \times 10^{-2} \text{ s}^{-1}$ ;  $D_2/r_c^2 = 1.2 \times 10^{-4} \text{ s}^{-1}$ ;  $D_1/D_2 = 125$ ; ratio of single-site Langmuir parameter  $b_2/b_1 = 1.07$ . The continuous solid

lines are the calculations using Equation (40). The dashed lines are the calculations using uncoupled flux equation (54).

Figure 54. Simulations of transient uptake of  $C_3H_6(1)/C_3H_8(2)$  within crystals of ZIF-8 at 303 K. The three sets of simulations include thermodynamic coupling. In the simulations  $D_2/r_c^2 = 1.2 \times 10^{-4} \text{ s}^{-1}$ . The ratios  $D_1/D_2$  have three different values: 2, 10, and 125. The continuous solid lines are transient uptake simulations use Equation (40).

Figure 55. Simulations of transient desorption of  $C_3H_6(1)/C_3H_8(2)$  from crystals of ZIF-8 at 303 K. Initially, the crystals are equilibrated by exposing the crystals to bulk gas mixture with  $p_1 = 50$  kPa;  $p_2 = 50$  kPa. This equilibrated crystal is then brought into contact with a bulk gas phase with  $p_1 = 10$  kPa;  $p_2 = 10$  kPa. In the simulations  $D_2/r_c^2 = 1.2 \times 10^{-4}$  s<sup>-1</sup>. The ratio  $D_1/D_2 = 125$ . The continuous solid lines are transient uptake simulations use Equation (40). The dashed lines are the calculations using uncoupled flux equation (54).

Figure 56. Transient uptake inside MFI extrudate exposed to a gas phase 2MP(1)/22DMB(2) mixture at 473 K. The partial pressures of the components in the bulk gas phase are  $p_1 = 22.7$  kPa;  $p_2 = 26.6$  kPa. These conditions correspond to Run 17 of Jolimaître et al.<sup>59</sup> Diffusional effects are quantified with  $D_{2MP}/r_c^2 = 5 \times 10^{-3} \text{ s}^{-1}$ ;  $D_{22DMB}/r_c^2 = 6.25 \times 10^{-5} \text{ s}^{-1}$ . The continuous solid lines represent uptake simulations include thermodynamic coupling using the flux relations Equation (40). The dashed lines represent uptake simulations ignoring thermodynamic coupling and use uncoupled flux equation (54). The input data are provided in Table 6.

Figure 57. Transient development of 2MP and 22DMB loadings along the radius of MFI extrudate (center, r = 0; surface of crystal,  $r = r_c$ ) monitored at different times from start of the uptake. The input data are the same as in Figure 56.

Figure 58. Transient development of "corrected" loadings  $q_1(\mu_1 - \mu_1^0)/RT = \Gamma_{11}q_1 + \Gamma_{12}q_2$ , and  $q_2(\mu_2 - \mu_2^0)/RT = \Gamma_{21}q_1 + \Gamma_{22}q_2$  of 2MP(1), and 22DMB(2) along the radius of MFI extrudate (center, r = 0; surface of crystal,  $r = r_c$ ) monitored at different times from start of the uptake. The input data are the same as in Figure 56.

Figure 59. Comparison of transient breakthrough experimental data for 2MP(1)/22DMB(2) mixtures (Run 17) of Jolimaître et al.<sup>59</sup> with transient breakthrough simulations. The partial pressures of the components in the bulk gas phase at the inlet are  $p_1 = 22.7$  kPa;  $p_2 = 26.6$  kPa. The parameter values are: L = 0.795 m; voidage of bed,  $\varepsilon = 0.4$ ; interstitial gas velocity, v = 0.019 m/s. The continuous solid lines represent breakthrough simulations include thermodynamic coupling using the flux relations Equation (40). The dashed lines represent breakthrough simulations ignoring thermodynamic coupling and using uncoupled flux equation (54). The input data are provided in Table 6.

Figure 60. Transient uptake inside MFI extrudate exposed to a gas phase 2MB(1)/2MP(2)/22DMB(3) mixture at 473 K. The partial pressures of the components in the bulk gas phase are  $p_1 = 81$  kPa;  $p_2 = 177$  kPa;  $p_2 = 106$  kPa. These conditions correspond to Run 20 of Jolimaître et al.<sup>59</sup> Diffusional effects are quantified with  $D_{2MB}/r_c^2 = 7.5 \times 10^{-3}$  s<sup>-1</sup>;  $D_{2MP}/r_c^2 = 5 \times 10^{-3}$  s<sup>-1</sup>;  $D_{22DMB}/r_c^2 = 6.25 \times 10^{-5}$  s<sup>-1</sup>. The continuous solid lines represent uptake simulations include thermodynamic coupling using the flux

relations Equation (40). The dashed lines represent uptake simulations ignoring thermodynamic coupling and use uncoupled flux equation (54). The input data are provided in Table 6.

Figure 61. Comparison of transient breakthrough experimental data for 2MB(1)/2MP(2)/22DMB(3) mixtures (for Run 20) of Jolimaître et al.<sup>59</sup> with transient breakthrough simulations. The parameter values are: L = 0.795 m; voidage of bed,  $\varepsilon = 0.4$ ; interstitial gas velocity, v = 0.0198 m/s. The continuous solid lines represent breakthrough simulations include thermodynamic coupling using the flux relations Equation (40). The dashed lines represent breakthrough simulations ignoring thermodynamic coupling and using uncoupled flux equation (54). The input data are provided in Table 6.

Figure 62. Experimental data of Saint-Remi et al.<sup>61</sup> for transient uptake of ethanol/1-propanol mixtures within SAPO-34, that is the structural analog of CHA zeolite.

Figure 63. Breakthrough experimental data of Remy et al.<sup>64</sup> for separation of ethanol/1-propanol mixtures in a fixed bed adsorber packed with SAPO-34.

Figure 64. (a) Simulations of transient uptake of ethanol(1)/1-propanol(2) mixtures within CHA crystals, exposed to binary fluid mixtures with partial fugacities  $f_{\text{ethanol}} = f_{1-\text{propanol}} = 0.5$  MPa. The pure component isotherms were fitted to the experimental data using the dual-site Langmuir Freundlich parameters as specified in Table 9. The adsorption equilibrium is calculated using the IAST, using the pure component fit parameters in Table 9. The Maxwell-Stefan diffusivities:  $D_{ethanol}/r_c^2 = 4 \times 10^{-3} \text{ s}^{-1}$ ;

 $D_{1-propanol}/r_c^2 = 4 \times 10^{-5} \text{ s}^{-1}$ . The continuous solid lines are the calculations with flux relations Equation (40). The dashed lines are the calculations neglecting thermodynamic coupling and using uncoupled flux equation (54). (b) Transient development of loadings of ethanol(1), and 1-propanol(2) inside CHA crystal.

Figure 65. Breakthrough simulations for ethanol/1-propanol mixtures in a fixed bed adsorber packed with CHA. The continuous solid lines are the calculations with flux relations Equation (40). The adsorption equilibrium is calculated using the IAST, using the pure component fit parameters in Table 9.

Figure 66. Simulation of transient permeation of  $C_3H_6(1)/C_3H_8(2)$  mixture across ZIF-8 membrane at 303 K. The diffusivity data used are:<sup>57</sup>  $\rho D_1/\delta = 1.39 \times 10^{-4}$  kg m<sup>-2</sup> s<sup>-1</sup>,  $\rho D_2/\delta = 1.11 \times 10^{-6}$  kg m<sup>-2</sup> s<sup>-1</sup>;  $D_1/D_2 = 125$ ; ratio of single-site Langmuir parameter  $b_2/b_1 = 1.07$ ; membrane thickness  $\delta = 10$  µm; partial pressures in upstream membrane compartment,  $p_{10} = p_{20} = 50$  kPa. The downstream compartment is placed under vacuum, i.e.  $p_{1\delta} = p_{2\delta} \approx 0$ . The loadings at the upstream face are:  $q_{10} = 1.937$  mol kg<sup>-1</sup>,  $q_{20} = 2.067$  mol kg<sup>-1</sup>. The loadings at the downstream face are:  $q_{1\delta} = q_{2\delta} \approx 0$ . The plots show the normalized fluxes  $N_1/(\rho q_{10} D_1/\delta)$ , and  $N_2/(\rho q_{20} D_2/\delta)$  as a function of the square root of time. The continuous solid lines are the calculations using Equation (40). The dashed lines are the calculations using uncoupled flux equation (54).

Figure 67. Transient development of  $C_3H_6(1)$ , and  $C_3H_8(2)$  loadings along the membrane thickness (upstream face, z = 0; downstream face,  $z = \delta$ ) monitored at different times from start of the permeation. Input data are the same as in Figure 66.

Figure 68. Transient development of "corrected" loadings  $q_1(\mu_1 - \mu_1^0)/RT = \Gamma_{11}q_1 + \Gamma_{12}q_2$ , and  $q_2(\mu_2 - \mu_2^0)/RT = \Gamma_{21}q_1 + \Gamma_{22}q_2$  of C<sub>3</sub>H<sub>6</sub>(1), and C<sub>3</sub>H<sub>8</sub>(2) along the membrane thickness (upstream face, z = 0; downstream face,  $z = \delta$ ) monitored at different times from start of the permeation. Input data are the same as in Figure 66.

Figure 69. (a) Experimental data of Geus et al.<sup>67</sup> for transient permeation 50/50 CH<sub>4</sub>/nC<sub>4</sub>H<sub>10</sub> mixture across an MFI membrane. (b) Transient simulations of CH<sub>4</sub>(1)/nC<sub>4</sub>H<sub>10</sub>(2) membrane permeation. The diffusivity data used are:  $\rho D_1 / \delta = 7.18 \times 10^{-3}$  kg m<sup>-2</sup> s<sup>-1</sup>,  $\rho D_2 / \delta = 7.18 \times 10^{-4}$  kg m<sup>-2</sup> s<sup>-1</sup>;  $D_1 / D_2 = 10$ ;  $D_1 / D_{12} = 2$ ; membrane thickness  $\delta = 200$  µm; partial pressures in upstream membrane compartment,  $p_{10} = p_{20} = 50$  kPa. The downstream compartment is placed under vacuum, i.e.  $p_{1\delta} = p_{2\delta} \approx 0$ . The loadings at the upstream face are:  $q_{10} = 0.0063$  mol kg<sup>-1</sup>,  $q_{20} = 1.638$  mol kg<sup>-1</sup>. The loadings at the downstream face are:  $q_{1\delta} = q_{2\delta} \approx 0$ . The plot shows the normalized fluxes  $N_1 / (\rho q_{10} D_1 / \delta)$ , and  $N_2 / (\rho q_{20} D_2 / \delta)$  as a function of the square root of time. The continuous solid lines are the calculations using Equation (39), including both correlations and thermodynamic coupling. The dashed lines are the calculations using uncoupled flux equation (54). The mixture adsorption equilibrium is calculated using IAST; the pure component isotherms are specified in Table 8.

Figure 70. Transient development of CH<sub>4</sub>(1), and nC<sub>4</sub>H<sub>10</sub>(2) loadings along the MFI membrane thickness (upstream face, z = 0; downstream face,  $z = \delta$ ) monitored at different times from start of the permeation. Input data are the same as in Figure 69.

Figure 71. Transient development of "corrected" loadings  $q_1(\mu_1 - \mu_1^0)/RT = \Gamma_{11}q_1 + \Gamma_{12}q_2$ , and  $q_2(\mu_2 - \mu_2^0)/RT = \Gamma_{21}q_1 + \Gamma_{22}q_2$  of CH<sub>4</sub>(1), and nC<sub>4</sub>H<sub>10</sub>(2) along the MFI membrane thickness (upstream face, z = 0; downstream face,  $z = \delta$ ) monitored at different times from start of the permeation. Input data are the same as in Figure 69.

Figure 72. (a) Experimental data of Bakker<sup>68</sup> for transient permeation 95/5 H<sub>2</sub>/nC<sub>4</sub>H<sub>10</sub> mixture across an MFI membrane. (b) Transient simulations of membrane permeation. The diffusivity data used are:  $\rho D_1/\delta = 0.359$  kg m<sup>-2</sup> s<sup>-1</sup>,  $\rho D_2/\delta = 7.18 \times 10^{-4}$  kg m<sup>-2</sup> s<sup>-1</sup>;  $D_1/D_2 = 500$ ;  $D_1/D_{12} = 5$ ; membrane thickness  $\delta = 200$  µm; partial pressures in upstream membrane compartment,  $p_{10} = 95$  kPa;  $p_{20} = 5$  kPa. The downstream compartment is placed under vacuum, i.e.  $p_{1\delta} = p_{2\delta} \approx 0$ . The loadings at the upstream face are:  $q_{10} = 0.00235$  mol kg<sup>-1</sup>,  $q_{20} = 1.555$  mol kg<sup>-1</sup>. The loadings at the downstream face are:  $q_{1\delta} = q_{2\delta} \approx 0$ . The plot shows the normalized fluxes  $N_1/(\rho q_{10} D_1/\delta)$ , and  $N_2/(\rho q_{20} D_2/\delta)$  as a function of the square root of time. The continuous solid lines are the calculations using either Equation (39), including both correlations and thermodynamic coupling, or Equation (40) that include thermodynamic coupling but neglect correlations. The dashed lines are the calculations using uncoupled flux equation (54). The mixture adsorption equilibrium is calculated using IAST; the pure component isotherms are specified in Table 8. Figure 73. Transient development of H<sub>2</sub>(1), and nC<sub>4</sub>H<sub>10</sub>(2) loadings along the MFI membrane thickness (upstream face, z = 0; downstream face,  $z = \delta$ ) monitored at different times from start of the permeation. Input data are the same as in Figure 72.

Figure 74. Transient development of "corrected" loadings  $q_1(\mu_1 - \mu_1^0)/RT = \Gamma_{11}q_1 + \Gamma_{12}q_2$ , and  $q_2(\mu_2 - \mu_2^0)/RT = \Gamma_{21}q_1 + \Gamma_{22}q_2$  of H<sub>2</sub>(1), and nC<sub>4</sub>H<sub>10</sub>(2) along the MFI membrane thickness (upstream face, z = 0; downstream face,  $z = \delta$ ) monitored at different times from start of the permeation. Input data are the same as in Figure 72.

Figure 75. (a, b) Experimental data of Matsufuji et al.<sup>69</sup> for transient permeation of (a) nC6/2MP, and (b) nC6/23DMB mixtures across an MFI membrane.

Figure 76. Simulation of transient permeation of nC6(1)/2MP(2) mixture across an MFI membrane at 300 K. The diffusivity data used are:  $\rho D_1 / \delta = 1.8 \times 10^{-4}$  kg m<sup>-2</sup> s<sup>-1</sup>,  $\rho D_2 / \delta = 1.8 \times 10^{-6}$  kg m<sup>-2</sup> s<sup>-1</sup>;  $D_1 / D_2 = 100$ ; membrane thickness  $\delta = 50$  µm; partial pressures in upstream membrane compartment,  $p_{10} = p_{20} = 1.3$  Pa. The downstream compartment is placed under vacuum, i.e.  $p_{1\delta} = p_{2\delta} \approx 0$ . The loadings at the upstream face are:  $q_{10} = 0.458$  mol kg<sup>-1</sup>,  $q_{20} = 0.32$  mol kg<sup>-1</sup>. The loadings at the downstream face are:  $q_{1\delta} = q_{2\delta} \approx 0$ . The plots show the normalized fluxes  $N_1 / (\rho q_{10} D_1 / \delta)$ , and  $N_2 / (\rho q_{20} D_2 / \delta)$  as a function of the square root of time. The continuous solid lines are the calculations using Equation (40). The dashed lines are the calculations using uncoupled flux equation (54). The isotherm data are provided in Table 5. The mixture adsorption equilibrium is determined using the IAST.

Figure 77. Transient development of nC6(1), and 2MP(2) loadings along the MFI membrane thickness (upstream face, z = 0; downstream face,  $z = \delta$ ) monitored at different times from start of the permeation. The partial pressures in upstream membrane compartment,  $p_{10} = p_{20} = 1.3$  Pa. Input data are the same as in Figure 76.

Figure 78. Transient development of "corrected" loadings  $q_1(\mu_1 - \mu_1^0)/RT = \Gamma_{11}q_1 + \Gamma_{12}q_2$ , and  $q_2(\mu_2 - \mu_2^0)/RT = \Gamma_{21}q_1 + \Gamma_{22}q_2$  of nC6(1), and 2MP(2) along the MFI membrane thickness (upstream face, z = 0; downstream face,  $z = \delta$ ) monitored at different times from start of the permeation. The partial pressures in upstream membrane compartment,  $p_{10} = p_{20} = 1.3$  Pa. Input data are the same as in Figure 76.

Figure 79. (a, b) Experimental data of Matsufuji et al.<sup>70</sup> for transient permeation of (a) 50/50 mxylene/p-xylene, and (b) 24/51/25 *p*-xylene/*m*-xylene/*o*-xylene mixtures across MFI membrane at 303 K.

Figure 80. Simulation of transient permeation of 50/50 m-xylene(1)/p-xylene(2) mixture across an MFI membrane at 300 K. The diffusivity data used are:  $\rho D_1 / \delta = 3.59 \times 10^{-5} \text{ kg m}^{-2} \text{ s}^{-1}$ ,  $\rho D_2 / \delta = 1.8 \times 10^{-4} \text{ kg} \text{ m}^{-2} \text{ s}^{-1}$ ;  $D_1 / D_2 = 0.1$ ; membrane thickness  $\delta = 50 \text{ }\mu\text{m}$ ; partial pressures in upstream membrane compartment,  $p_{10} = 10 \text{ Pa}$ ;  $p_{20} = 10 \text{ Pa}$ . The downstream compartment is placed under vacuum, i.e.  $p_{1\delta} = p_{2\delta} \approx 0$ . The pure component isotherms are obtained from the molecular simulation data (for the

orthorhombic (often denoted as ORTHO) MFI framework) of Chempath et al;<sup>71</sup> see Table 10. The mixture adsorption equilibrium is determined using the mixed gas Langmuir model. The loadings at the upstream face are:  $q_{10} = 0.438$  mol kg<sup>-1</sup>,  $q_{20} = 0.219$  mol kg<sup>-1</sup>. The plots show the normalized fluxes  $N_1/(\rho q_{10} D_1/\delta)$ , and  $N_2/(\rho q_{20} D_2/\delta)$  as a function of the square root of time. The continuous solid lines are the calculations using Equation (40). The dashed lines are the calculations using uncoupled flux equation (54).

Figure 81. Simulation of transient permeation of nC4(1)/iC4(2) mixture across an MFI membrane at 300 K. The diffusivity data used are:  $\rho D_1 / \delta = 1.45 \times 10^{-4}$  kg m<sup>-2</sup> s<sup>-1</sup>,  $\rho D_2 / \delta = 6.92 \times 10^{-5}$  kg m<sup>-2</sup> s<sup>-1</sup>;  $D_1 / D_2$  = 20; membrane thickness  $\delta = 200$  µm; partial pressures in upstream membrane compartment,  $p_{10} = 5$  kPa;  $p_{20} = 95$  kPa. The downstream compartment is placed under vacuum, i.e.  $p_{1\delta} = p_{2\delta} \approx 0$ . The loadings at the upstream face are:  $q_{10} = 0.8072$  mol kg<sup>-1</sup>,  $q_{20} = 0.7706$  mol kg<sup>-1</sup>. The loadings at the downstream face are:  $q_{1\delta} = q_{2\delta} \approx 0$ . The plots show the normalized fluxes  $N_1 / (\rho q_{10} D_1 / \delta)$ , and  $N_2 / (\rho q_{20} D_2 / \delta)$  as a function of the square root of time. The continuous solid lines are the calculations using Equation (40). The dashed lines are the calculations using uncoupled flux equation (54). The isotherm data are provided in Table 5. The mixture adsorption equilibrium is determined using the IAST.

Figure 82. Simulation of transient permeation of water(1)/ethanol(2) mixture across a DDR membrane at 300 K. The diffusivity data used are:  $\rho D_1 / \delta = 6.8 \times 10^{-4} \text{ kg m}^{-2} \text{ s}^{-1}$ ,  $\rho D_2 / \delta = 6.8 \times 10^{-5} \text{ kg m}^{-2} \text{ s}^{-1}$ ;  $D_1 / D_2 = 10$ ; membrane thickness  $\delta = 200 \text{ }\mu\text{m}$ ; partial pressures in upstream membrane compartment,  $p_{10} = 5 \text{ kPa}$ ;  $p_{20} = 95 \text{ kPa}$ . The downstream compartment is placed under vacuum, i.e.  $p_{1\delta} = p_{2\delta} \approx 0$ . The loadings at the upstream face are:  $q_{10} = 0.344 \text{ mol kg}^{-1}$ ,  $q_{20} = 1.744 \text{ mol kg}^{-1}$ . The loadings at the ESI 95 downstream face are:  $q_{1\delta} = q_{2\delta} \approx 0$ . The plots show the normalized fluxes  $N_1/(\rho q_{10} D_1/\delta)$ , and  $N_2/(\rho q_{20} D_2/\delta)$  as a function of the square root of time. The isotherm data are provided in Table 11. The mixture adsorption equilibrium is determined using the IAST. The continuous solid lines are the calculations using Equation (40). The dashed lines are the calculations using uncoupled flux equation (54).

Figure 83. Transient development of water(1)/ethanol(2) mixture across the DDR membrane thickness (upstream face, z = 0; downstream face,  $z = \delta$ ) monitored at different times from start of the permeation. Input data are the same as in Figure 82.

Figure 84. Simulation of transient permeation of water(1)/ethanol(2) mixture across a LTA-4A membrane at 333 K. The diffusivity data used are:  $\rho D_1 / \delta = 7.65 \times 10^{-3} \text{ kg m}^{-2} \text{ s}^{-1}$ ,  $\rho D_2 / \delta = 7.65 \times 10^{-4} \text{ kg m}^{-2} \text{ s}^{-1}$ ;  $D_1 / D_2 = 10$ ; membrane thickness  $\delta = 200 \text{ }\mu\text{m}$ ; partial pressures in upstream membrane compartment,  $p_{10} = 50 \text{ Pa}$ ;  $p_{20} = 950 \text{ Pa}$ . The downstream compartment is placed under vacuum, i.e.  $p_{1\delta} = p_{2\delta} \approx 0$ . The loadings at the upstream face are:  $q_{10} = 0.9774 \text{ mol kg}^{-1}$ ,  $q_{20} = 2.025 \text{ mol kg}^{-1}$ . The loadings at the downstream face are:  $q_{1\delta} = q_{2\delta} \approx 0$ . The plots show the normalized fluxes  $N_1 / (\rho q_{10} D_1 / \delta)$ , and  $N_2 / (\rho q_{20} D_2 / \delta)$  as a function of the square root of time. The isotherm data are provided in Table 12. The mixture adsorption equilibrium is determined using the IAST. The continuous solid lines are the calculations using flux Equation (40). The dashed lines are the calculations using uncoupled flux equation (54).

Figure 85. Transient development of water(1)/ethanol(2) mixture across the LTA-4A membrane thickness (upstream face, z = 0; downstream face,  $z = \delta$ ) monitored at different times from start of the permeation. Input data are the same as in Figure 84.

Figure 86. Calculation of the (steady-state) effectiveness factor,  $\eta$ , for uptake inside MFI catalyst exposed to a gas phase 2MP(1)/22DMB(2) mixture at 473 K, carrying out the isomerization reaction 2MP(1)  $\rightleftharpoons$  22DMB(2). The partial pressures of the components in the bulk gas phase are  $p_1 = 22.7$  kPa;  $p_2 = 26.6$  kPa. The ratio of rate constants  $k_1/k_2 = 2$ . The values of the rate constant  $k_1$  are varied. The zero-loading diffusivities  $D_1(0) = 2 \times 10^{-14}$  m<sup>2</sup> s<sup>-1</sup>;  $D_1(0) = 2.5 \times 10^{-16}$  m<sup>2</sup> s<sup>-1</sup>. The radius of the crystal  $r_c$  $= 2 \ \mu$ m. The Thiele modulus is calculated from  $\phi = \frac{r_c}{3} \sqrt{\frac{k_1}{D_1(0)} + \frac{k_2}{D_2(0)}}$ . The calculations using the

five different scenarios are based on the analytical solutions provided by Baur and Krishna.<sup>21</sup>

Figure 87. Transient uptake inside MFI catalyst exposed to a gas phase 2MP(1)/22DMB(2) mixture at 473 K, carrying out the isomerization reaction 2MP(1)  $\rightleftharpoons$  22DMB(2). The partial pressures of the components in the bulk gas phase are  $p_1 = 22.7$  kPa;  $p_2 = 26.6$  kPa. These conditions correspond to Run 17 of Jolimaître et al.<sup>59</sup> Diffusional effects are quantified with  $D_{2MP}/r_c^2 = 5 \times 10^{-3} \text{ s}^{-1}$ ;  $D_{22DMB}/r_c^2 = 6.25 \times 10^{-5} \text{ s}^{-1}$ . The reaction rate constants are  $k_1 = 0.0011 \text{ s}^{-1}$ ,  $k_2 = 0.00055 \text{ s}^{-1}$ ; these rate constants are taken from Baur and Krishna.<sup>21</sup> The continuous solid lines represent uptake simulations include thermodynamic coupling using the flux relations (40). The dashed lines represent uptake simulations ignoring thermodynamic coupling and use uncoupled flux equation (54). The input data are provided in Table 6.

Figure 88. Transient development of 2MP(1) and 22DMB(2) loadings along the radius of MFI catalyst (center, r = 0; surface of crystal,  $r = r_c$ ), carrying out the isomerization reaction 2MP(1) $\rightleftharpoons$  22DMB(2), monitored at different times from start of the uptake. The input data are the same as in Figure 87.

Figure 89. Transient development of "corrected" loadings  $q_1(\mu_1 - \mu_1^0)/RT = \Gamma_{11}q_1 + \Gamma_{12}q_2$ , and  $q_2(\mu_2 - \mu_2^0)/RT = \Gamma_{21}q_1 + \Gamma_{22}q_2$  of 2MP(1), and 22DMB(2) along the radius of MFI catalyst (center, r = 0; surface of crystal,  $r = r_c$ ), carrying out the isomerization reaction 2MP(1) $\rightleftharpoons$  22DMB(2), monitored at different times from start of the uptake. The input data are the same as in Figure 87.

Figure 90. Transient breakthrough simulations for fixed bed 2MP(1)/22DMB(2) isomerization reactor with MFI extrudates, carrying out the isomerization reaction  $2MP(1) \rightleftharpoons 22DMB(2)$ . The parameter values are: L = 0.795 m; voidage of bed,  $\varepsilon = 0.4$ ; interstitial gas velocity, v = 0.019 m/s. The continuous solid lines represent breakthrough simulations include thermodynamic coupling using the flux relations (40). The dashed lines represent breakthrough simulations ignoring thermodynamic coupling and using uncoupled flux equation (54). The input data are provided in Table 6. Figure 91. Transient uptake inside MFI catalyst exposed to a gas phase nC6(1)/3MP(2)/22DMB(3)mixture at 362 K, carrying out the isomerization reaction  $nC6(1) \neq 3MP(2) \neq 22DMB(3)$ . The partial pressures of the components in the bulk gas phase are  $p_1 = 2$  kPa;  $p_2 = 40$  kPa,  $p_3 = 60$  kPa. Diffusional effects are quantified with  $D_{nC6}/r_c^2 = 2 \times 10^{-2} \text{ s}^{-1}$ ;  $D_{3MP}/r_c^2 = 2 \times 10^{-3} \text{ s}^{-1}$ ;  $D_{22DMB}/r_c^2 = 1 \times 10^{-3} \text{ s}^{-1}$ . All three M-S diffusivities are assumed to follow the loading dependence  $D_i(\theta) = D_i(0)\theta_V$ . The reaction rate constants are  $k_{f1} = 0.009 \text{ Pa}^{-1} \text{ s}^{-1}$ ,  $k_{b1} = 0.007 \text{ Pa}^{-1} \text{ s}^{-1}$ ;  $k_{f2} = 0.009 \text{ Pa}^{-1} \text{ s}^{-1}$ ,  $k_{b2} = 0.007 \text{ Pa}^{-1} \text{ s}^{-1}$ . The continuous solid lines represent uptake simulations include thermodynamic coupling using the flux relations (40). The dashed lines represent uptake simulations ignoring thermodynamic coupling and use uncoupled flux equation (54). The isotherm input data are provided in Table 14.

Figure 92. Transient uptake inside MFI catalyst exposed to a gas phase m-xylene(1)/p-xylene(2) mixture at 303 K, carrying out the isomerization reaction m – xylene(1) $\rightleftharpoons$  p – xylene(2). The partial pressures of the components in the bulk gas phase are  $p_1 = 10$  Pa;  $p_2 = 10$  Pa. Diffusional effects are quantified with  $D_1/r_c^2 = 2 \times 10^{-5} \text{ s}^{-1}$ ;  $D_2/r_c^2 = 1 \times 10^{-4} \text{ s}^{-1}$ . The reaction rate constants are  $k_1 = 0.001 \text{ s}^{-1}$ ,  $k_2 = 0.0005 \text{ s}^{-1}$ . The continuous solid lines represent uptake simulations include thermodynamic coupling using the flux relations (40). The dashed lines represent uptake simulations ignoring thermodynamic coupling and use uncoupled flux equation (54). The isotherm input data are provided in Table 10.

Figure 93. Transient uptake inside MFI catalyst exposed to a gas phase ethene(1)/benzene(2)/ethylbenzene(3) mixture at 653 K, carrying out the ethylation reaction

ethene(1) + benzene(2)  $\rightleftharpoons$  ethylbenzene(3). The partial pressures of the components in the bulk gas

phase are  $p_1 = 800$  kPa;  $p_2 = 200$  kPa,  $p_3 = 0$  kPa. Diffusional effects are quantified with  $D_{ethene}/r_c^2 = 1 \times 10^{-3}$  s<sup>-1</sup>;  $D_{benzene}/r_c^2 = 2 \times 10^{-5}$  s<sup>-1</sup>;  $D_{ethylbenzene}/r_c^2 = 1 \times 10^{-5}$  s<sup>-1</sup>. The continuous solid lines represent uptake simulations include thermodynamic coupling using the flux relations (40). The dashed lines represent uptake simulations ignoring thermodynamic coupling and use uncoupled flux equation (54). The isotherm input data are provided in Table 15.

Figure 94. Transient uptake inside MFI catalyst exposed to a gas phase ethane(1)/ethene(2)/hydrogen(3) mixture at 653 K, carrying out the dehydrogenation reaction ethane(1)  $\rightleftharpoons$  ethene(2) + hydrogen(3). The partial pressures of the components in the bulk gas phase are  $p_1 = 0.2$  MPa;  $p_2 = 0.1$  MPa,  $p_3 = 1$  MPa. Diffusional effects are quantified with  $D_{ethane}/r_c^2 = 2.5 \times 10^{-4} \text{ s}^{-1}$ ;  $D_{ethene}/r_c^2 = 5 \times 10^{-4} \text{ s}^{-1}$ ;  $D_{hydrogen}/r_c^2 = 1.25 \times 10^{-2} \text{ s}^{-1}$ . The continuous solid lines represent uptake simulations include thermodynamic coupling using the flux relations (40). The dashed lines represent uptake simulations ignoring thermodynamic coupling and use uncoupled flux equation (54). The isotherm input data are provided in Table 15.



# Unary diffusivities vs spreading pressure



## Unary diffusivities vs spreading pressure







#### **Discretization strategies**



### Model for membrane permeation



### Degree of correlations in MFI membrane




# Degree of correlations in MFI zeolite



#### Figure S10 Degree of correlations in MFI zeolite



0.01

0.001

2

3

4

5

Upstream total pressure,  $p_{to}$  / bar

 $\rho D_1 / \delta = 64 \text{ kg m}^{-2} \text{ s}^{-1}$  $\rho D_2 / \delta = 3.2 \text{ kg m}^{-2} \text{ s}^{-1}$ 

6

7

8

#### Fixed bed adsorber



#### **DDR** landscape

Figure S12



Structural information from: C. Baerlocher, L.B. McCusker, Database of Zeolite Structures, International Zeolite Association, http://www.iza-structure.org/databases/

To convert from molecules per unit cell to mol kg^-1, multiply by 0.06936. The pore volume is 0.182 cm<sup>3</sup>/g.



# Figure S13 **DDR pore landscapes**



#### $\ensuremath{\textbf{DDR}}$ window and pore dimensions



The window dimensions calculated using the van der Waals diameter of framework atoms = 2.7 Å are indicated above by the arrows.

	DDR
a /Å	24.006
b/Å	13.86
c/Å	40.892
Cell volume / Å <sup>3</sup>	13605.72
conversion factor for [molec/uc] to [mol per kg Framework]	0.0693
conversion factor for [molec/uc] to [kmol/m <sup>3</sup> ]	0.4981
ho [kg/m3]	1759.991
MW unit cell [g/mol(framework)]	14420.35
$\phi$ , fractional pore volume	0.245
open space / ų/uc	3333.5
Pore volume / cm <sup>3</sup> /g	0.139
Surface area /m²/g	350.0
DeLaunay diameter /Å	3.65



#### Unary isotherms



#### Mixture adsorption equilibrium



#### Matrix of thermodynamic factors



#### Significance of thermodynamic coupling



#### Crystal geometry





Spherical crystal model

Hexagonal crystal used in experiments

#### Diffusivities



# 1:1 CO<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> time-averaged uptake in $DDR^{S22}$



Figure S23

# 2:1 $CO_2/C_2H_6$ uptake in DDR



Figure S24

# 3:1 $CO_2/C_2H_6$ uptake in DDR



Simulations with:  $D_1/D_2 = 1333;$ 

 $D_{1}/r_{c}^{2} = 0.125 \text{ s}^{-1}$ 

surface

 $t = 0.2 \, s$ 

= 0.47 s = 0.77 s

= 1.1 s = 2.1 s = 99.8 s

= 300.3 s t = 807.5 s

0.6 1.0 0.6 100 0.4 60 0.2 100 0.2 100 0.2 100

0.0

DDR; 298 K;

1.0

0.8

0.6

0.4

0.2

dimensionless distance,  $r/r_{\rm c}$ 

 $p_{co2} = 20 \text{ kPa};$ р<sub>с2н6</sub> = 20 кРа;

### 1:1 $CO_2/C_2H_6$ transient development of loadings in DDR crystal



<sup>-</sup>surface

DDR; 298 K; p<sub>CO2</sub> = 40 kPa;

р<sub>С2Н6</sub> = 20 kРа;

Simulations with:  $D_1/D_2 = 100;$ 

 $D_1/r_2^2 = 0.00937 \text{ s}^{-1}$ 

### $2:1 \text{ CO}_2/\text{C}_2\text{H}_6$ transient development of loadings in DDR crystal



### 3:1 CO<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> transient development of loadings in DDR crystal





### 2:1 CO<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> transient development of "corrected" loadings in DDR crystal





### 3:1 CO<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> transient development of "corrected" loadings in DDR crystal







# $2:1 \text{ CO}_2/\text{C}_2\text{H}_6$ transient development of loadings in DDR crystal:

**Experimental data** 







#### Figure S33 Transient breakthrough in DDR fixed bed



Dimensionless time,  $\tau = t v / L$ 



To convert from molecules per unit cell to mol  $kg^{\text{-}1},$  multiply by 0.0733. The pore volume is 0.245 cm³/g.





#### LTA-4A

The window dimension calculated using the van der Waals diameter of framework atoms = 2.7 Å is indicated above by the arrow. The pore landscape is also shown in the above picture.

Note that the Na<sup>+</sup> ions partially block the windows and therefore the diffusivities in LTA-4A are significantly lower than that for all-silica LTA.

#### Figure S34

# N<sub>2</sub>/CH<sub>4</sub> mixture uptake in LTA-4A Figure S35



## Transient development of loadings in LTA-4A crystal





Transient development of "corrected" loadings in LTA-4A crystal

Figure S37





# Transient uptake of O<sub>2</sub>/N<sub>2</sub> in CMS Figure S38



# Transient development of loadings in CMS particle



#### MFI pore landscape

DeLaunay diameter /Å

	MFI
a /Å	20.022
b/Å	19.899
c /Å	13.383
Cell volume / Å <sup>3</sup>	5332.025
conversion factor for [molec/uc] to [mol per kg Framework]	0.1734
conversion factor for [molec/uc] to [kmol/m <sup>3</sup> ]	1.0477
ho [kg/m3]	1796.386
MW unit cell [g/mol(framework)]	5768.141
$\phi$ , fractional pore volume	0.297
open space / Å <sup>3</sup> /uc	1584.9
Pore volume / cm <sup>3</sup> /g	0.165
Surface area /m²/g	487.0

Structural information from: C. Baerlocher, L.B. McCusker, Database of Zeolite Structures, International Zeolite Association, http://www.iza-structure.org/databases/



5.16

#### MFI pore dimensions

10 ring channel of MFI viewed along [100]



10 ring channel of MFI viewed along [010]

# nC6/2MP mixture uptake in MFI Figure S42







## **Transient development** of loadings in MFI crystal

nC6 loading / molec uc<sup>-1</sup>



nC6/2MP mixture; MFI; T = 298 K;

=1.23 s

= 10.2 s

t =50.6 s

t = 102 s *t* = 132 s *t* = 832 s

2499. (2.2) × (2.2) 1000000

= 5 \$ = 5.9 s

surface

 $D_1 / D_2 = 100;$ 

 $D_2/r_c^2 = 1.6 \times 10^{-4} \text{ s}^{-1}$ 

0

nC6/2MP mixture;

MFI; T = 298 K;  $p_1 = p_2 = 0$  Pa to 1.3 E

1.0

0.8

0.6

0.4

0.2

## Transient development of "corrected" loadings in MFI


### Transient nC4/iC4 uptake in MFI







# Figure S48 Transient n-heptane/benzene uptake in NaX





# Figure S49 Transient N2/CH4 uptake in BaETS-4



### Transient uptake in Activated Carbon



### **ZIF-8** pore landscapes

The ZIF-8 =  $Zn(methylimidazole)_2$  structure was taken from

R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe, O.M. Yaghi, High-Throughput Synthesis of Zeolitic Imidazolate Frameworks and Application to  $CO_2$  Capture, Science 319 (2008) 939-943.





There are 2 cages per unit cell. The volume of one ZIF-8 cage is 1168 Å<sup>3</sup>, significantly larger than that of a single cage of DDR (278 Å<sup>3</sup>), or FAU (786 Å<sup>3</sup>).

Flexible windows 3.3 Å

### **ZIF-8** dimensions



This plot of surface area versus pore dimension is determined using a combination of the DeLaunay triangulation method for pore dimension determination, and the procedure of Düren for determination of the surface area.

	ZIF-8
a /Å	16.991
b/Å	16.991
c /Å	16.991
Cell volume / Å <sup>3</sup>	4905.201
conversion factor for [molec/uc] to [mol per kg Framework]	0.3663
conversion factor for [molec/uc] to [kmol/m <sup>3</sup> ]	0.7106
ho [kg/m3]	924.253
MW unit cell [g/mol(framework)]	2730.182
$\phi$ , fractional pore volume	0.476
open space / ų/uc	2337.0
Pore volume / cm <sup>3</sup> /g	0.515
Surface area /m²/g	1164.7
DeLaunay diameter /Å	3.26

### Propene/propane uptake in ZIF-8





### Propene/propane uptake in ZIF-8





### Propene/propane uptake in ZIF-8



### Transient 2MP/22DMB uptake in MFI





### 2MP/22DMB loading profiles in MFI Figure S57



## <sup>Figure S58</sup> 2MP/22DMB corrected loading profiles in MFI



### Figure S59 Transient 2MP/22DMB breakthrough in fixed bed of MFI extrudates



time / min

### Transient 2MB/2MP/22DMB uptake in MFI





# Transient 2MB/2MP/22DMB breakthrough in fixed bed of MFI extrudates



time / min

### Transient ethanol/1-propanol uptake in SAPO-34





# Figure S63 Transient breakthrough of 1-alcohols in SAPO-34





### Transient ethanol/1-propanol uptake in CHA

(a)





# Transient ethanol/1-propanol breakthrough in fixed bed of CHA



Dimensionless time,  $\tau = t v / L$ 

### $C_{3}H_{6}/C_{3}H_{8}$ permeation across ZIF-8 membrane<sup>Figure S66</sup>



C<sub>3</sub>H<sub>6</sub>, including thermodynamic coupling C<sub>3</sub>H<sub>8</sub>, including thermodynamic coupling C<sub>3</sub>H<sub>6</sub>, neglecting thermodynamic coupling C<sub>3</sub>H<sub>8</sub>, neglecting thermodynamic coupling





# Figure S67 $C_3H_6/C_3H_8$ loading profiles in membrane



# $C_{3}H_{6}/C_{3}H_{8}$ corrected loading profiles in membrane



# $CH_4/nC_4H_{10}$ permeation: MFI membrane



(a)





## $CH_4/nC_4H_{10}$ loading profiles: MFI membrane





dimensionless distance,  $z / \delta$ 

### CH<sub>4</sub>/nC<sub>4</sub>H<sub>10</sub> corrected loading profiles<sup>Figure S71</sup> MFI membrane





### $H_2/nC_4H_{10}$ permeation: MFI membrane



### H<sub>2</sub>/nC<sub>4</sub>H<sub>10</sub> loading profiles: MFI membrane





### H<sub>2</sub>/nC<sub>4</sub>H<sub>10</sub> corrected loading profiles:<sup>Figure S74</sup> MFI membrane





### nC6/2MP and nC6/23DMB permeation across MFI membrane: Matsufuji





 $t / \min$ 

### nC6/2MP permeation across MFI membrane<sup>S76</sup>



# rigure S77 nC6/2MP loading profiles in MFI membrane



### nC6/2MP corrected loading profiles in MFI membrane



### Xylenes permeation across MFI membrane S79



t / min

(b) 24/51/25 p-xylene/m-xylene/o-xylene mixture: MFI; T = 303 Kp-xylene m-xylene o-xylene 3.0 2.5  $Flux / 10^{-7}$  mol m<sup>-2</sup> s<sup>-1</sup> 2.0 1.5 1.0 0.5 0.0 5 10 15 20 25 30 0

*t /* min

o-xylene is preferentially located at the intersections of MFI



m-xylene is preferentially located at the intersections of MFI



p-xylene can locate along the channels MFI






3.0

# water/ethanol pervaporation DDR membrane



#### Figure S83 Water/ethanol loading profiles in DDR membrane





# water/ethanol pervaporation LTA-4A membrane



The snapshot shows water and ethanol molecules in the cages of LTA.



#### Water/ethanol loading profiles in LTA-4Aure S85 membrane





# Effectiveness factor for 2MP/22DMB<sup>Figure S86</sup> diffusion/reaction in MFI catalyst



# Transient 2MP/22DMB diffusion/reaction in MFI catalyst





## 2MP/22DMB loading profiles in MFI catality st S88





## Transient 2MP/22DMB breakthrough in fixed bed MFI adsorber-reactor



time / min

# Transient nC6/3MP/22DMB diffusion/reaction in MFI catalyst



 $nC6(1) \rightleftharpoons 3MP(2) \rightleftharpoons 22DMB(3)$ 



# Transient m-X/p-X diffusion/reaction in MFI catalyst

m-xylene, including thermodynamic coupling p-xylene, including thermodynamic coupling m-xylene, neglecting thermodynamic coupling p-xylene, neglecting thermodynamic coupling Spatial-averaged component uptake / mol kg $^{-1}$ 0.4 0.3 Simulations with: 0.2  $D_{2}/D_{1} = 5;$  $D_2/r_c^2 = 0.0001 \text{ s}^{-1}$ MFI catalyst; 303 K; 0.1  $k_1 = 0.001 \text{ s}^{-1}; k_1/k_2 = 2$  $p_1 = p_2 = 10 \text{ Pa}$ 1 1 1 0.0 0 2 8 Δ 10 6 square root of time,  $t^{1/2} / \min^{1/2}$ 

The diffusivity of p-xylene (= component 2) is assumed to be 5 times higher than that of m-xylene (= component 1)

 $m - xylene(1) \not \ge p - xylene(2)$ 



# Transient ethene/benzene/ethylbenzene diffusion/reaction in MFI catalyst



Spatial-averaged component uptake / mol kg $^{-1}$ 

#### Figure S94

# Transient ethane/ethene/hydrogen diffusion/reaction in MFI catalyst

