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Diffusion of CH_4 and CO_2 in MFI, CHA and DDR zeolites

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Abstract

Molecular dynamics simulations were carried out to determine the self-diffusivities of CH_4 and CO_2 both for pure components and in 50–50 mixtures for a range of molar loadings in MFI, CHA and DDR zeolites. In CHA and DDR zeolites, that consist of cages separated by narrow windows, the inter-cage hopping of molecules occur practically independent of one another and, consequently, the diffusivities of pure components are the same as in the mixture. In sharp contrast, in MFI that consists of intersecting channels, the more mobile species is slowed down significantly in the mixture.

1. Introduction

The separation of carbon dioxide (CO_2) from natural gas, consisting predominantly of methane (CH_4), is an important practical problem. One method for separation of CO_2 from CH_4 is to exploit the subtle differences in the molecular dimensions of the two molecules (see Fig. 1) by allowing these molecules to adsorb and diffuse through zeolites. MFI, CHA and DDR zeolite membranes are currently being investigated for this separation task [1–3]. For economical separations CH_4 needs to be retained at high pressures; consequently the molecular loadings within the zeolite are expected to be high. For development, and design of a zeolite membrane based separation process it is essential to have a proper understanding of the diffusion characteristics of the pure components, and mixtures, within the zeolites for a wide range of loadings. The major objective of this Letter is to gain the required insights by means of Molecular Dynamics (MD) simulations. For the interpretation of the MD simulation results, Grand Canonical Monte Carlo (GCMC) simulations were carried out to determine the adsorption isotherms of the pure components.

2. GCMC and MD simulation methodologies

The adsorption isotherms for CH_4 and CO_2 in MFI, CHA and DDR were computed using Monte Carlo (MC) simulations in the grand canonical (GC) ensemble. The crystallographic data are available elsewhere [4]. The MFI, CHA and DDR zeolite lattices are rigid during simulations, with static atomic charges that are assigned by choosing $q_{Si} = +2.05$ and $q_O = -1.025$, following the work of Calero et al. [5]. CH_4 molecules are described with a united atom model, in which each molecule is treated as a single interaction center [6]. CO_2 molecules are taken linear and rigid, with bond length C–O of 1.16Å and partial charges distributed around each molecule to reproduce experimental quadrupole moment. The interaction between adsorbed molecules is described with Coulombic and Lennard-Jones terms. The parameters for methane are taken from Dubbeldam et al. [7]. For CO_2 we use the 3LJ3CB.EPM2 potential [8]. The Lennard-Jones parameters for CH_4–zeolite and CO_2–zeolite interactions are taken from Dubbeldam et al. [7] and Makrodimitris et al. [9], respectively. The Lennard-Jones potentials are shifted and cut at 12 Å. The number of unit cells in the simulation box was chosen such that

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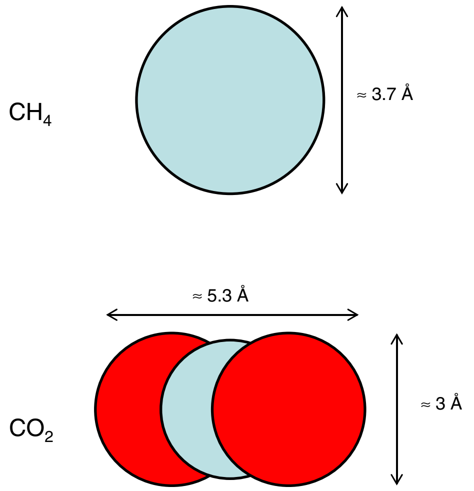

Fig. 1. Cartoon showing the approximate molecular dimensions of CH_4 and CO_2.

the minimum length in each of the coordinate directions was larger than 24 Å. The detailed validation of the force fields used for CH_4 and for CO_2 are available elsewhere [7,10]. Periodic boundary conditions were employed. Further GCMC and MD simulation details are available in earlier publications [5,7,11–15].

The self-diffusivities, $D_{\mathrm{i,self}}$, were computed by analyzing the mean square displacement of each component:

$$D_{\mathrm{i,self}} = \frac{1}{2N_{\mathrm{i}}} \lim_{\Delta t \to \infty} \frac{1}{\Delta t} \left\langle \left(\sum_{l=1}^{N_{\mathrm{i}}} (\mathbf{r}_{l,\mathrm{i}}(t+\Delta t) - \mathbf{r}_{l,\mathrm{i}}(t))^2 \right) \right\rangle \tag{1}$$

In this expression N_{i} represents the number of molecules of species i, respectively, and $\mathbf{r}_{l,\mathrm{i}}(t)$ is the position of molecule l of species i at any time t. For DDR the reported diffusivities are the averages in x and y directions $Đ = (Đ_x + Đ_y)/2$. For other cases (MFI, CHA) the average values calculated according to $Đ = (Đ_x + Đ_y + Đ_z)/3$ are presented. In all cases reported here, the MSD values were linear in t.

3. Results and discussion

Fig. 2a compares the GCMC simulated isotherms for CH_4 and CO_2 in MFI with the experimental isotherm data of Zhu et al. [1] and Golden and Sircar [16]. The GCMC simulation data are obtained in terms of fugacities, and these are plotted on the x-axis rather than pressures. Up to the range of fugacities used in the experimental isotherms, 1 MPa, there is good agreement between the experiments and GCMC simulations, pointing to the validity of the force field used in the simulations. The saturation capacities $q_{\mathrm{i,sat}}$ of CH_4 and CO_2 are determined to be 4 and 5.9 mol/kg, respectively. Fig. 2b presents the MD simulation results for the self-diffusivities both for pure components, and the values in a 50–50 mixture as a function of the total loading in MFI. The $D_{\mathrm{i,self}}$ values of both species tends to reduce to zero as $q_{\mathrm{i,sat}}$ is approached. Since all the vacant 'sites' within the zeolite framework are nearly all occupied, most of molecular jumps will be unsuccessful and the molecule will invariably return to its original site, resulting in vanishingly small diffusivities. The $D_{\mathrm{i,self}}$ for CH_4 is higher than that of CO_2 for the entire range of loadings; the lower value for CO_2 can be attributed to the fact that it is a longer molecule (Fig. 1), and its jumps along the channel structure of MFI occur at a slower rate than that of the more compact CH_4. Snapshots obtained from the GCMC simulations at a pressure of 10^6 Pa, show the location of the molecules along the straight and zig-zag channels; see Fig. 2c,d. The CO_2 molecules appear to align themselves perpendicular to the channels; this could be an explanation for the lower diffusivity.

From Fig. 2b we note that the $D_{\mathrm{i,self}}$ of the more mobile CH_4 species is significantly lower in the mixture than for pure species, when compared at the same total loading q. This is to be contrasted with the fact that $D_{\mathrm{i,self}}$ of the tardier CO_2 is practically the same in the mixture as for the pure component. The presence of the tardier molecule within the MFI channels tends to slow down the more mobile species; this effect is due to correlations in the molecular jumps [11,17,18]. The corresponding speeding up of CO_2 due to the presence of CH_4 appears to be negligibly small.

Fig. 3a compares the GCMC simulated isotherms in CHA with the experimental isotherm data of Li et al. [19] for SAPO-34, an isotype of CHA. Up to the range of fugacities used in the experimental isotherms, 120 kPa, there is good agreement between the experiments and GCMC simulations. The $D_{\mathrm{i,self}}$ of both species tends to reduce to zero as $q_{\mathrm{i,sat}}$ is approached; see Fig. 3b. In contrast to the results for MFI, in CHA the $D_{\mathrm{i,self}}$ for CO_2 is higher than that of CH_4 for the entire range of loadings. The reason for this can be gleaned from the snapshots in Fig. 3c,d. The windows separating two cages of CHA are only about 3.8 Å wide and can accommodate only one molecule at a time. CO_2 is a more slender molecule than CH_4, and the energy barrier for inter-cage hopping is lower than that for methane. The self-diffusivity of CH_4 *increases* with q in the range 0–6 mol/kg, before reducing, inevitably to zero value as $q_{\mathrm{i,sat}}$ is approached. The reason for the increase in $D_{\mathrm{i,self}}$ is the reduction of the free energy barrier for inter-cage hopping of molecules with intra-cage loading, as has been explained in some detail by Beerdsen et al. [20–22]. For CO_2 the diffusivity remains practically independent of q in the range 0–4 mol/kg, before reducing to vanishing values at $q_{\mathrm{i,sat}}$. Apparently, the influence of intra-cage loading of CO_2 does not lead to a reduction in the free energy barrier.

Comparing the pure component diffusivities to those in the mixture we observe that for a range of loadings up to 5 mol/kg there is no speeding-up of CH_4 or slowing-down of CO_2 in the mixture; the inter-cage hopping of molecules are practically independent of one another.

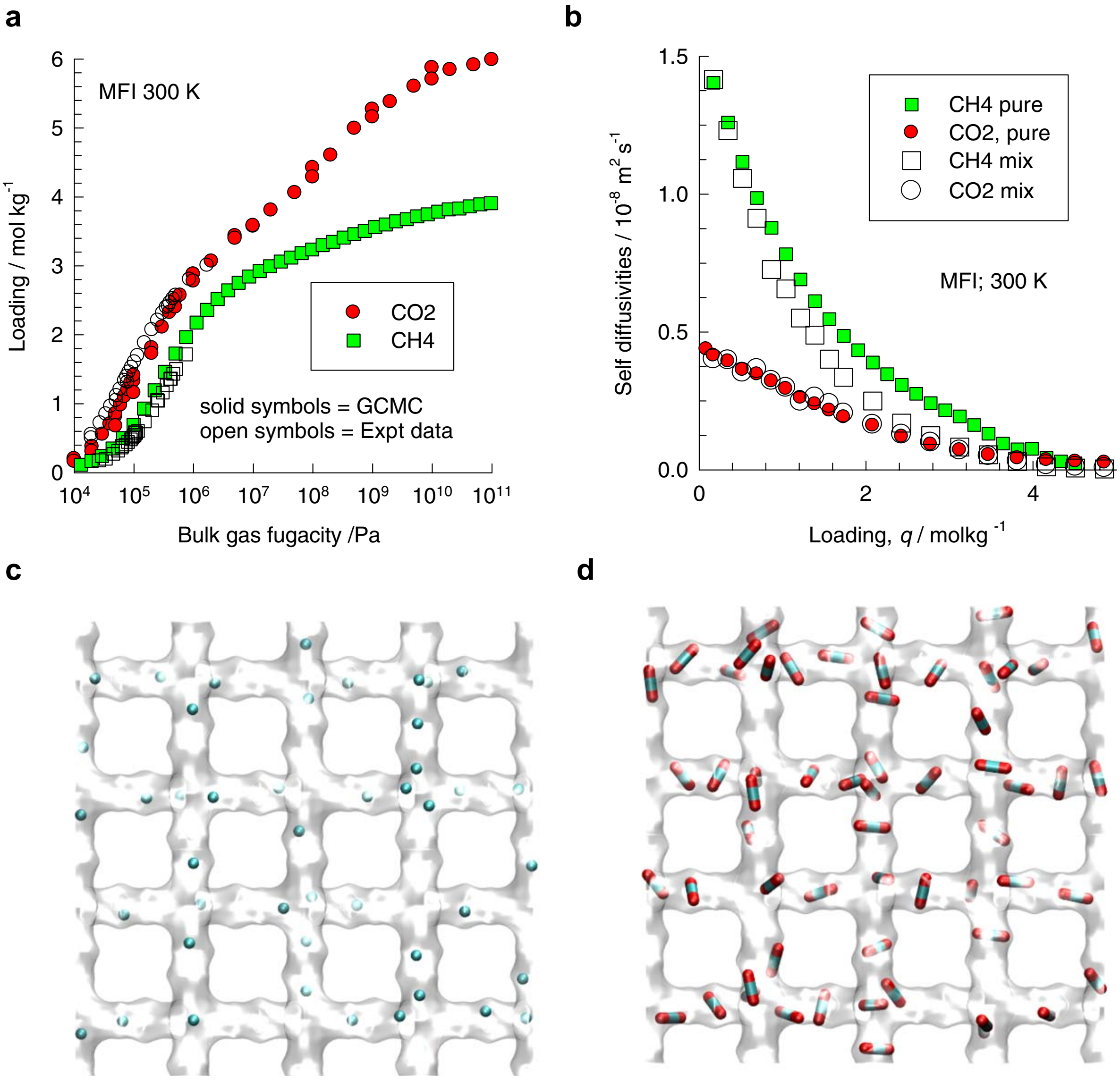

Fig. 2. (a) Sorption isotherm data for CH_4 and CO_2 in MFI at 300 K. The filled symbols are GCMC simulation results. The open symbols are experimental data of Zhu et al. [1] and Golden and Sircar [16]. (b) MD simulations of self-diffusivities of CH_4 and CO_2 obtained for both pure components and in a 50–50 mixture plotted against the total molar loading, q. Snapshots showing the location of (c) CH_4 and (d) CO_2 molecules along the straight and zig-zag channels at 1000 MPa.

Fig. 4a present the GCMC simulated isotherm data in DDR. Fig. 4b presents the MD simulation results for the self-diffusivities; the $D_{i,self}$ of both species tends to reduce to zero as $q_{i,sat}$ is approached. The loading dependence of the diffusivities of both species in DDR is analogous to that observed for CHA. Interestingly, there is approximately a 50-fold increase in $D_{i,self}$ of CH_4 as q is increased to 3 mol/kg. The reduction in the free energy barrier for inter-cage hopping of CH_4 appears to be more strongly influenced by intra-cage loading in DDR than in CHA. One possible reason could be that the window size of DDR is 3.6 Å, slightly smaller than that in CHA. Up to a loading of 3.5 mol/kg the self-diffusivities of pure components are virtually the same as in the mixture and inter-cage hops are independent of one another. There is no speeding-up of CH_4 or slowing-down of CO_2 in the mixture. The narrow windows of DDR allow only one molecule to jump across cages at a time; see snapshots in Fig. 4c,d.

Within the framework of the Maxwell-Stefan diffusion formulation for mixture diffusion in zeolites, the MD simulation results presented above indicate that the binary exchange coefficient $Đ_{ij}$ can be taken to be infinitely large for CHA and DDR membranes, in agreement with the conclusion reached by independent considerations and analysis of experimental data [10].

The ratio of $D_{i,self}$ of CO_2 to that of CH_4 in the 50–50 mixture is plotted against the loading q in Fig. 5a. We

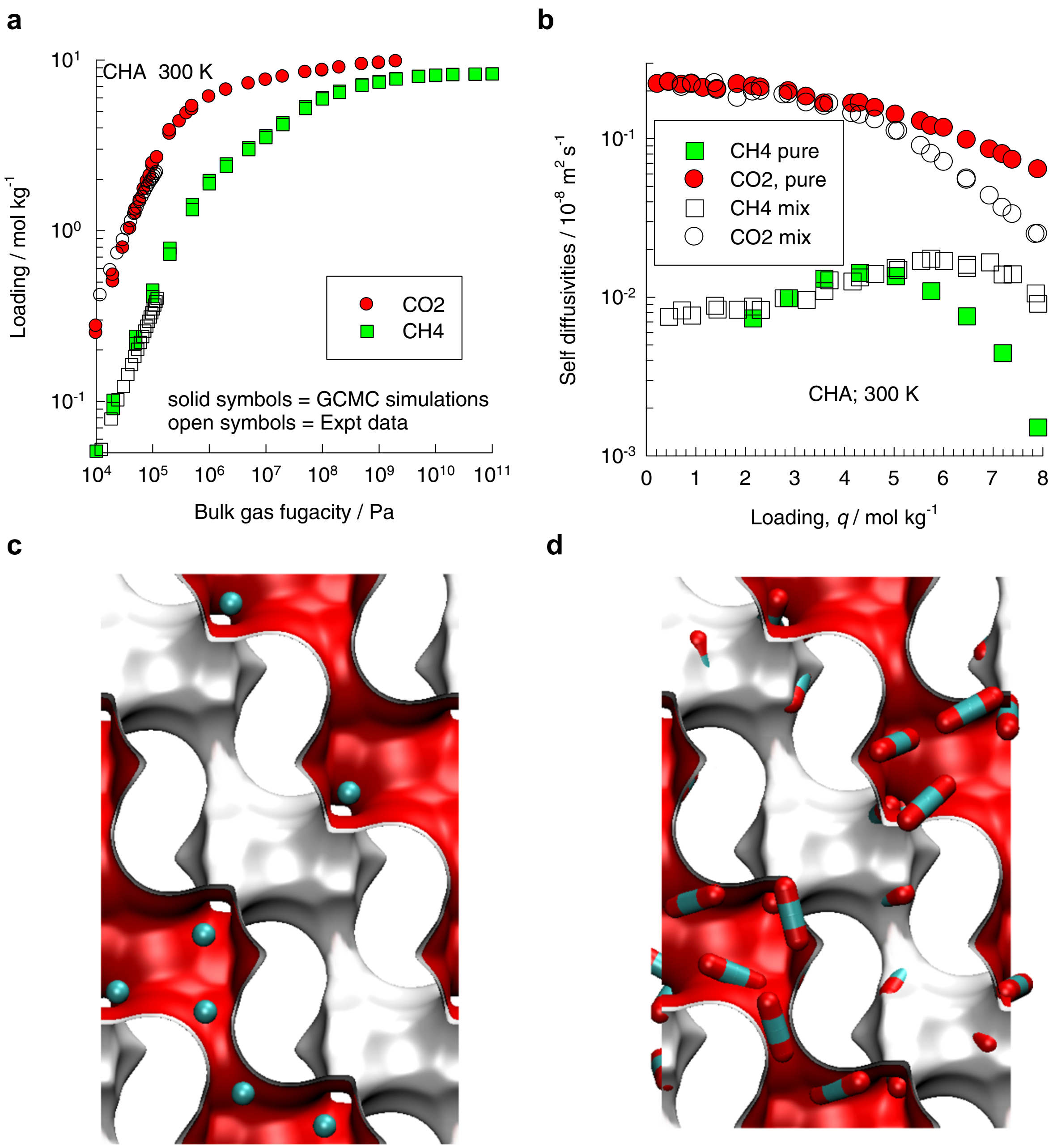

Fig. 3. (a) Sorption isotherm data for CH_4 and CO_2 in CHA at 300 K. The filled symbols are GCMC simulation results. The open symbols are experimental data of Li et al. [19] for SAPO-34, an isotype of CHA. (b) MD simulations of self-diffusivities of CH_4 and CO_2, obtained for both pure components and in a 50–50 mixture plotted against the total molar loading, q. Snapshots showing the location of (c) CH_4 and (d) CO_2 molecules at 1000 MPa.

see that diffusion selectivity is strongly dependent on both the loading and choice of zeolite; the variation is about five orders of magnitude. CHA and DDR zeolites are both promising candidates for separation, and are clearly superior to MFI. Experimental data on transport coefficients, $\rho \text{Đ}_{\mathrm{i}}/\rho$, i.e. the diffusivity times the zeolite density divided by the membrane film thickness have been determined for MFI, CHA and DDR membranes at 300 K by Krishna et al. [10] using published experimental data [1–3]; the ratio of these transport coefficients for CO_2 and CH_4 are plotted in Fig. 5b. We note that the hierarchy of the diffusion selectivity values, as well as the dependence of the selectivity on the total loading is in broad agreement with those obtained from MD simulated self diffusivities.

4. Conclusions

In this Letter the self-diffusivities $D_{\mathrm{i,self}}$ of CH_4 and CO_2 have been determined in three different zeolites,

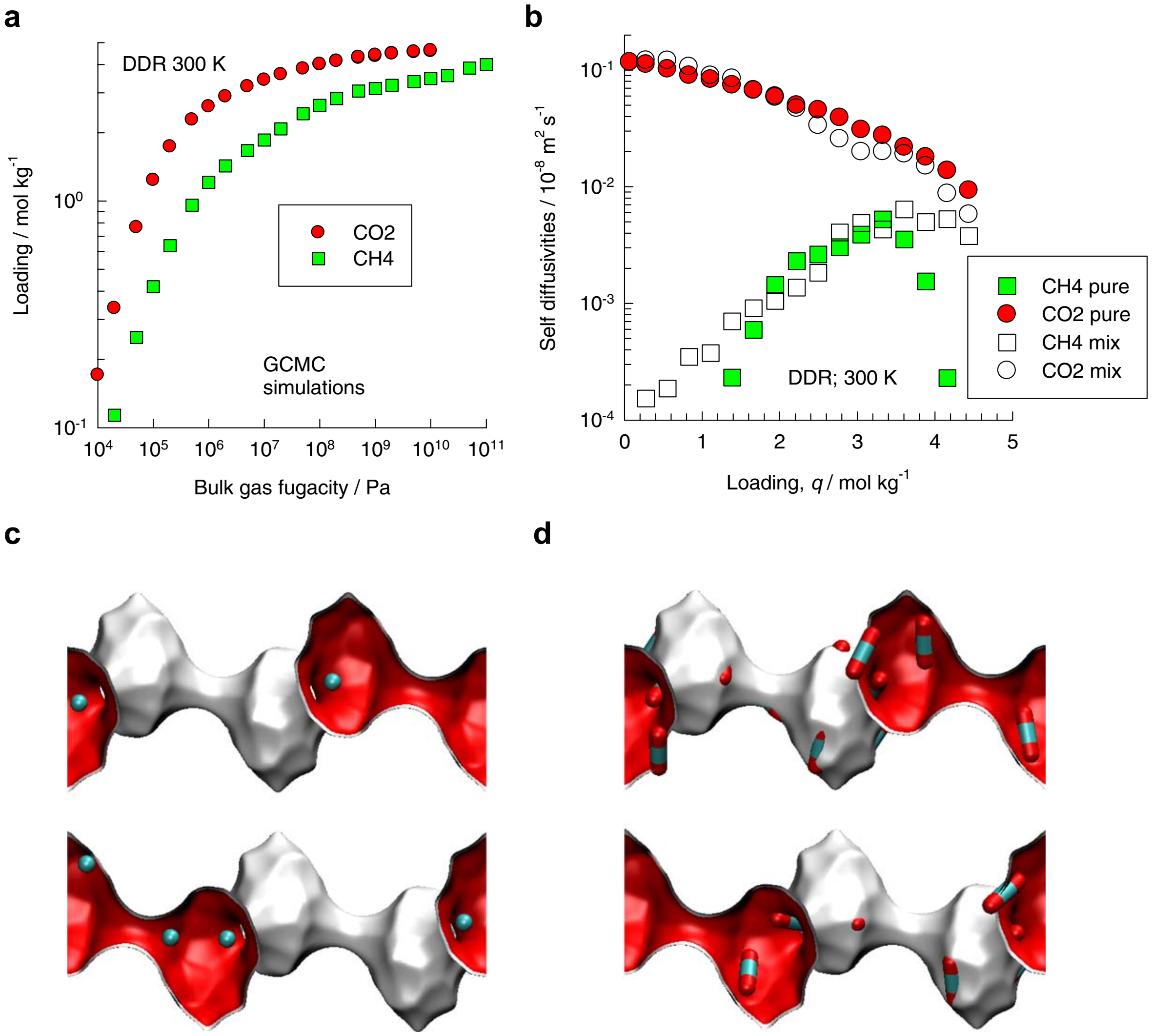

Fig. 4. (a) Sorption isotherm data for CH_4 and CO_2 in DDR at 300 K. (b) MD simulations of self-diffusivities of CH_4 and CO_2 obtained for both pure components and in a 50–50 mixture plotted against the total molar loading, q. Snapshots showing the location of (c) CH_4 and (d) CO_2 molecules at 1000 MPa.

MFI, CHA and DDR. The following conclusions can be drawn from the results presented in this Letter:

(1) In all three zeolites the $D_{\mathrm{i,self}}$ of any species reduces to zero as the saturation loading $q_{\mathrm{i,sat}}$ is approached.
(2) In the intersecting channel structures of MFI, CO_2 has a lower diffusivity than CH_4 possibly due to a higher molecular length. In CHA and DDR, that consist of cages separated by narrow windows, the more slender CO_2 has the higher diffusivity.
(3) In CHA and DDR there is a significant increase in $D_{\mathrm{i,self}}$ of CH_4 for a range of loadings; this increase is due to the reduction in the free energy barrier for inter-cage hopping of molecules [22].
(4) In the intersecting channel structures of MFI correlation effects cause a significant slowing down of the faster diffusing species.
(5) For DDR, for loadings <3.5 mol/kg the self-diffusivities in the mixture are virtually the same as for pure components indicating that the inter-cage hopping of molecules through the narrow windows separating the cages occur independently of one another. This conclusion is also true for CHA for a limited range of loadings <5 mol/kg; beyond this loading the CO_2 appears to get slowed down by the presence of the CH_4.
(6) On the basis of the results presented in Fig. 5 we note that the highest diffusion selectivity for separation is offered by either CHA and DDR, depending on the loading.

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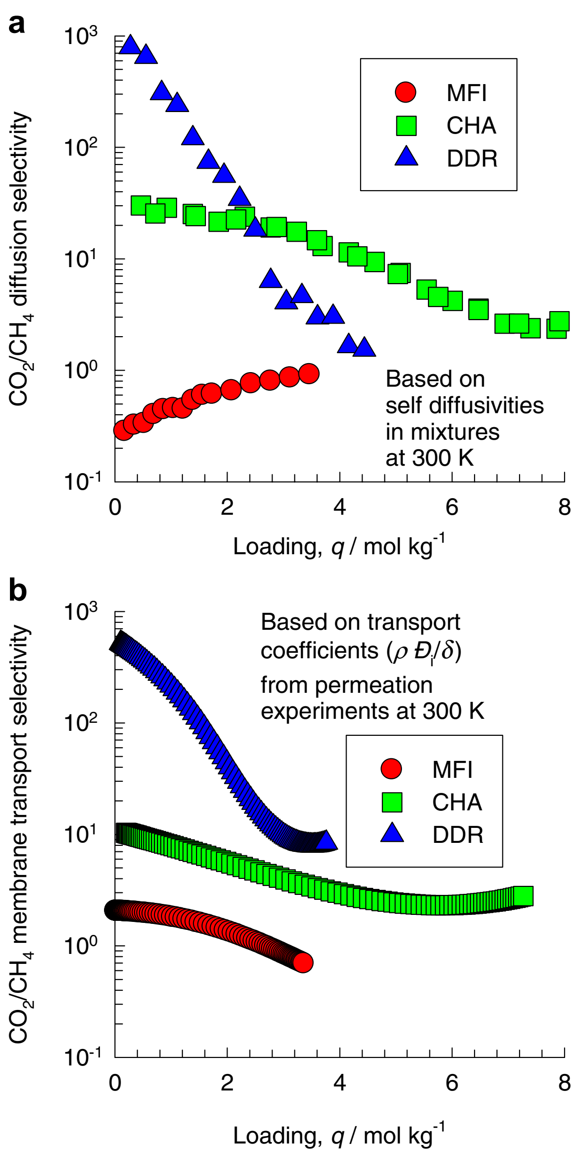

Fig. 5. (a) Diffusion selectivity, defined as the ratio of the self-diffusivity of CO_2 to that of CH_4 in a 50–50 mixture as a function of loading q for MFI, CHA and DDR zeolites. (b) Membrane transport selectivity calculated from information in Krishna et al. [10].

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