Self-diffusion of pure and mixed gases in mixed-linker zeolitic imidazolate framework-7-8 by high field diffusion NMR

Samuel Berens[a], Febrian Hillman[b], Hae-Kwon Jeong[b], Sergey Vasenkov[a],*

[a] Department of Chemical Engineering, University of Florida, Gainesville, FL, 32611, USA
[b] Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX, 77843, USA

ABSTRACT

Self-diffusion of pure gases including carbon dioxide, methane, ethylene, ethane, and xenon as well as selected two-component mixtures was studied in hybrid zeolitic imidazolate framework-7-8 (ZIF-7-8) crystals using pulsed field gradient (PFG) NMR. This material was formed by mixing 2-methylimidazolate (ZIF-8 linker) and bulkier benzimidazolate (ZIF-7 linker) in the same framework. The intracrystalline diffusion data measured in mixed-linker ZIF-7-8 was compared with the corresponding data in the parent ZIF-8 material. It was found that under the same or comparable experimental conditions the intracrystalline gas diffusion was always slower in ZIF-7-8 than in ZIF-8. This observation is consistent with the expected lower pore aperture size in ZIF-7-8 than in ZIF-8. At the same time, the ethane/ethylene diffusion selectivity was found to be similar in both ZIFs. It was also observed that for the pure studied gases larger than carbon dioxide the diffusivity ratios in ZIF-8 and ZIF-7-8 do not increase with increasing gas size at all loading pressures used. All these data are attributed to greater framework flexibility effects in ZIF-7-8 than ZIF-8. Such effects manifest themselves in a distortion and/or increase in the aperture size in the presence of large sorbates due to linker flexibility.

1. Introduction

Zeolitic imidazolate frameworks (ZIFs) are a subtype of metal organic frameworks (MOFs) which exhibit zeolite-like framework topologies [1]. ZIFs have been recognized for their ability to adsorb large quantities of gases as well as act as molecular sieves in the same manner as traditional aluminosilicates [2–9]. Mass transfer within ZIFs is limited by pore aperture sizes which can be commensurate to the size of molecules diffusing within the pores [2,4,5]. This makes ZIFs excellent candidates for separations applications in which similarly sized sorbates are sieved by a ZIF whose pore aperture size is comparable with the sorbate sizes.

Diffusion studies identifying and evaluating such potential for separations have been performed for a variety of sorbates in ZIF-8, the most well-studied ZIF, which is composed of Zn^{+2} metal ions and 2-methylimidazolate (mIm) linkers [1]. The separation potential related to diffusion can be quantified using a diffusion selectivity, i.e. diffusivity ratios under the same or similar conditions. CO_2 and CH_4 mixtures exhibit a notable diffusion selectivity in ZIF-8 owing to the larger kinetic diameter of CH_4 [8,10,11]. Larger hydrocarbons such as ethane and ethylene have been also found to have significant diffusion selectivity in ZIF-8 [4,12,13]. An even better diffusion selectivity than for

ethane/ethylene was observed for propane/propylene in ZIF-8 [14]. Apart from gases, ZIF-8 also has the capabilities to separate liquid compounds such as methanol/ethanol mixtures [15].

Despite the narrow crystallographic aperture size of the six-membered rings in ZIF-8 (~3.4 Å) [5], molecules with larger kinetic diameters such as propylene and propane are still able to enter and diffuse through the ZIF-8 framework [9]. This observation can be explained by the framework flexibility of the ZIF framework, which might result in the ability of the imidazolate linkers to "swing" to a greater degree in the presence of an adsorbed species. Framework flexibility effects can also explain the phenomenon in which species such as CH_4 diffuse faster at higher concentrations within ZIF-8; as the species deforms the framework, it can cause pore windows to open to a greater extent thereby increasing diffusivity for adsorbed molecules [16–19]. These flexibility effects have been further explored and validated for other sorbates such as ethane, ethylene, and Xe [20,21].

While other ZIFs with similar structures such as ZIF-11 and ZIF-90 have also been studied extensively for their sorption/diffusion properties [15,22], a more recent class of ZIFs whose sorbate diffusion properties have not yet been well investigated are mixed-linker ZIFs. These ZIFs utilize a combination of two different linkers to achieve intermediate properties of the ZIFs formed by either of the two parent

* Corresponding author.
E-mail address: svasenkov@che.ufl.edu (S. Vasenkov).

linkers [23–29]. A promising mixed-linker ZIF, ZIF-7-8, has been identified as a good potential candidate for optimized molecular sieving owing to the pore window tunability by mixing mIm (ZIF-8 linker) with bulkier benzimidazolate (bIm, ZIF-7 linker) [24,25]. Our initial diffusion study performed in ZIF-7-8 by pulsed field gradient (PFG) NMR for a single sorbate (ethane) was recently reported [30]. Ethane self-diffusivity was found to vary significantly between individual ZIF-7-8 crystals as observed by PFG NMR in combination with single crystal IR microscopy, a powerful complimentary technique used in this study by our collaborators. In the present work, we expand the initial PFG NMR diffusion study of ethane in ZIF-7-8 to other sorbates including ethylene, CO_2, and CH_4. These sorbates were chosen for the industrially relevant and challenging processes of separating ethane/ethylene and CO_2/CH_4. Utilizing high magnetic field strengths (14 and 17.6 T) as well as large magnetic field gradients (up to 25 Tm^{-1}), we evaluate the ability of ZIF-7-8 to change the gas self-diffusivity in comparison to the parent ZIF-8 material and alter diffusion selectivity for the studied sorbates. Furthermore, we report mixed gas diffusion studies to determine the effect of co-adsorption of sorbates on diffusion selectivity and to evaluate the role of the framework flexibility of ZIF-7-8 in sorbate diffusion.

2. Experimental

2.1. Materials

Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 98%, hereafter ZnN), 2-methylimidazole ($C_4H_5N_2$, 97%, hereafter mIm), benzimidazole ($C_7H_6N_2$, 98%, hereafter bIm), and sodium formate (HCOONa, 99%) were obtained from Sigma-Aldrich. Methanol (99.8%) and di-methylformamide (99.8%) were purchased from Alfa Aesar. All materials were used without any further purification. Single ^{13}C-enriched ethane (C_2H_6), double ^{13}C-enriched ethylene (C_2H_4), ^{13}C carbon dioxide (CO_2), ^{13}C methane (CH_4), and ^{129}Xe were selected as sorbates for diffusion studies in ZIF-8 and ZIF-7-8. All sorbates had > 99% isotopic purity (Sigma-Aldrich).

2.2. Synthesis of ZIF-8 and ZIF-7-8 and standard characterization

For synthesis of ZIF-8 crystals, a solution of 1.13 mmol of ZnN dissolved in 20 mL of methanol was poured to a solution of 1.01 mmol of mIm in 20 mL of methanol while continuously stirred for 1 min. The mixed solution was then transferred to a Teflon-lined steel autoclave to be reacted for 24 h at 50 °C in an oven. For ZIF-7-8, a solution of 3.34 mmol of ZnN in 20 mL of dimethylformamide was poured to a solution of 4.67 mmol of mIm, 0.35 mmol of bIm, and 1.66 mmol of sodium formate in 20 mL of methanol, and allowed to continuously stir for 1 min. The resulting solution was transferred to a Teflon-lined steel autoclave and placed in an oven for 2 h at 95 °C. For both ZIF-8 and ZIF-7-8, after the reaction in oven, the solution was cooled at room temperature for 2 h before opening the autoclave to collect the precipitates. The cooled solutions were then centrifuged at 8000 rpm for 10 min to obtain the powders. To wash the crystals, they were dispersed in 30 mL of methanol followed by centrifugation (8000 rpm for 10 min) for three times cycle. The washed ZIF-8 and ZIF-7-8 crystals were dried at 120 °C for 2 h prior to further characterization. The scanning electron microscopy (SEM) images of the ZIF-8 and ZIF-7-8 crystals as shown in Fig. S1 were obtained using JEOL JSM-7500F operating at acceleration voltage of 5 keV with working distance of 15 mm. The average crystal sizes of ZIF-8 and ZIF-7-8 were determined by averaging the width of 10 crystals observed by SEM. ZIF-8 and ZIF-7-8 samples had comparable spherical crystal diameters of 18 μm and 13 μm, respectively. Room temperature X-ray diffraction (XRD) analyses were performed to determine the crystal structure of the obtained ZIF-8 and ZIF-7-8 as shown in Fig. S2. Rigaku Miniflex II was used for XRD characterization using Cu-Kα radiation (λ = 1.5406 Å), scanned with step size of 0.02°. Ethane

and ethylene adsorption isotherms were performed on ZIF-8 and ZIF-7-8 on an ASAP 2010 (Micrometrics) (Fig. S3). ZIF-8 isotherms of the C_2 species match well with previously published isotherms [4].

2.3. NMR sample preparation

NMR diffusion studies were performed for two sorbate loadings corresponding to the sorbate loading pressures of around 7.8 and 0.8 bar. The samples were prepared by loading around 60 mg of ZIF sample into an NMR tube and degassing overnight (~10 h) in a custom-made vacuum system at 383 K and 0.080 mbar. Once the samples were made sorbate free via degassing and cooled down to room temperature, they were cryogenically loaded with a calculated amount of the desired gas necessary to achieve a pressure of around either 8 or 0.8 bar in the gas volume of a sealed sample tube. These calculations were based on the adsorption isotherms of ZIF-7-8 (Fig. S3) or ZIF-8 [31,32] and known free gas volume of the tube. Once the gas was cryogenically transferred into the tubes using liquid nitrogen, the tubes were flame-sealed, separated from the vacuum system, and kept for at least 12 h at 296 ± 1 K before NMR studies to ensure that the sorption equilibrium was reached.

In addition to diffusion of pure gases, diffusion of the following binary mixtures was investigated in ZIF-7-8: C_2H_6/C_2H_4, CO_2/CH_4, and CO_2/C_2H_6. The equimolar gas mixtures were cryogenically transferred into NMR sample tube using the same procedure as with the single sorbate samples. Similarly, the mixed gas samples were flame sealed upon loading with total loading pressures around 8.2 bar at 296 ± 1 K.

Pressure in the gas phase of NMR samples with ZIFs was obtained by comparing NMR signal intensities measured for the gas phase of these samples with the corresponding signal in the reference samples containing only gas (no porous material added) at a known pressure. Concentrations inside the ZIF beds were calculated through a mass balance taking into account the known mass of the gas cryogenically added to the sample tubes. Concentrations matched adsorption isotherms for C_2 species in ZIF-7-8 and ZIF-8 as seen in Fig. S3.

2.4. PFG NMR measurements

^{13}C and ^{129}Xe NMR measurements were performed on a 51 mm bore 14 T Avance III 600 MHz spectrometer (Bruker Biospin) and an 89 mm bore 17.6 T Avance III HD 750 MHz spectrometer. ^{13}C PFG NMR was used for measurements of hydrocarbon diffusion instead of more traditional ^{1}H PFG NMR because of our previous observations of much longer T_2 NMR times of ^{13}C than ^{1}H of hydrocarbons confined in ZIFs [22,30]. Only ^{129}Xe NMR measurements as well as a few selected ^{13}C NMR measurements were performed at 17.6 T. These selected measurements were done to verify the results obtain at 14 T in order to confirm the absence of any measurement artifacts under our experimental conditions. Under the conditions of our ^{13}C NMR measurements at 14 and 17.6 T the resonance frequencies were equal to 150.1 and 188.6 MHz, respectively. ^{129}Xe NMR measurements were performed at a resonance frequency of 208.6 MHz at 17.6 T. For each studied sorbate an NMR spectrum consisted of a single line. The following chemical shifts were observed: C_2H_6 (6 ppm), C_2H_4 (122 ppm), CO_2 (128 ppm), CH_4 (−8 ppm), and Xe (156 ppm in ZIF-7-8 and 152 ppm in ZIF-8). ^{13}C and ^{129}Xe NMR chemical shifts are referenced to 40% 1,4-dioxane in benzene-d_6 at 67 ppm and gas phase Xe at 0 ppm, respectively. Fig. S4 displays representative NMR spectra of all species studied adsorbed in ZIF-7-8 at around 8 bar.

Diffusion measurements were performed using a 13-interval PFG NMR pulse sequence with bipolar gradients and an added longitudinal eddy-current delay of ~6 ms [33–35]. Diffusivities (D) were derived from the signal attenuation (Ψ) which measures NMR signal magnitude, i.e. area of NMR lines (S) as a function of gradient strength (g) and can be written as:

$$\Psi = \frac{S(g)}{S(g \approx 0)} = \exp(-\frac{<r^2(t)> q^2}{6}) = \exp(-q^2 D t) \qquad (1)$$

where $q = 2\gamma g \delta$, γ is the gyromagnetic ratio, g is the gradient strength, δ is the effective gradient pulse length, t is diffusion time, and $<r^2(t)>$ denotes the mean square displacements (MSD). MSD is related to D and t through the Einstein relation:

$$<r^2(t)> = 6Dt \qquad (2)$$

Bipolar, sine and trapezoidal-shaped magnetic field gradients were generated using a *Diff30* diffusion probe (Bruker Biospin) at 14 T and a *Diff50* diffusion probe (Bruker Biospin) at 17.6 T. Gradient pulse durations (δ) ranged from 1.5 to 3.5 ms for both probes and had a maximum amplitude around 11 T/m for the *Diff30* and 20 T/m for the *Diff50*. Typical PFG NMR experiments had between 256 and 1024 scans for each gradient step, total experimental times between 1 and 5 h, and repetition delays between 1 and 4 s (set at minimum 1.5 times greater than the T_1 relaxation time). NMR spectra were measured using a single radiofrequency pulse sequence before and after diffusion measurements to confirm the absence of any changes in sorbate concentration over the time of the experiments (see Fig. S4 for representative spectra of all sorbates).

Longitudinal (T_1) relaxation measurements were performed using the standard inversion recovery sequence. Transverse (T_2) relaxation measurements were done using the 13-interval PFG NMR sequence by changing the time intervals during which the T_2 NMR relaxation takes place and keeping all other intervals constant as done in previous studies [36]. In all samples, there was no observed distribution of T_1 or T_2 relaxation times for the adsorbed sorbates. T_1 and T_2 relaxation times are shown in Tables S1 and S2. All NMR measurements were performed at 296 ± 1 K.

3. Results and discussion

Figs. 1 and 2 show ^{13}C PFG NMR attenuation curves for the diffusion of four gases in ZIF-7-8 at the high and low loadings corresponding to the loading pressure of around 7.8 and 0.8 bar at 296 ± 1 K,

respectively. Ethane attenuation curves were previously reported in Ref. [30] and are shown in Figs. 1 and 2 for comparison to other sorbates. Also shown for comparison are the corresponding measured attenuation curves in ZIF-8, which was used as a reference material. It is important to note that ^{13}C T_2 NMR relaxation times of small gas molecules in ZIF-7, another reference material for ZIF-7-8, were found to be too small for meaningful PFG NMR measurements [30]. PFG NMR measurements in ZIF-7-8 and ZIF-8 were performed for different diffusion times shown in the figures. It is seen that in contrast to the monoexponential attenuation behavior in agreement with Eq. (1) observed for ZIF-8 (linear in the semilogarithmic presentation of Figs. 1 and 2), all the attenuation curves measured for ZIF-7-8 exhibit deviations from a monoexponential decay. The absence of any measurement artifacts in the attenuation data at 14 T was confirmed by the measurements of the same sample under the same conditions at 17.6 T (see data for C_2H_6 in Fig. 1). Coinciding attenuation curves measured for C_2H_6 at the different field strength provide such confirmation. Despite the deviations from the monoexponential behavior, the attenuation curves measured for the same ZIF-7-8 sample at different diffusion times coincide, within uncertainty, in the presentation of Figs. 1 and 2. The results of the recently published study of ethane diffusion in the same ZIF-7-8 sample as that used in the current work show that the observed deviations from the monoexponential behavior originate from the existence of differences between sorbate diffusivities in different ZIF-7-8 crystals of the sample [30]. In particular, single crystal IR microscopy measurements of the ethane transport diffusivities reported in Ref. [30] were found to vary significantly (up to a factor of 4.4) between randomly selected individual ZIF-7-8 crystals, thereby indicating there is indeed heterogeneity in transport properties between individual crystals. This heterogeneity was attributed to the difference in the fractions of mIm and bIm linkers observed for different ZIF-7-8 crystals from the studied sample by single crystal IR microscopy. The deviations from monoexponential attenuation in Figs. 1 and 2 confirm that the distribution of self-diffusivities between crystals exists for all gaseous sorbates studied.

An effective (average) diffusivity in the samples exhibiting distribution over diffusion coefficients can be obtained by fitting the initial

Fig. 1. ^{13}C PFG NMR attenuation curves at high sorbate loadings corresponding to a loading pressure of 7.8 ± 0.8 bar at 296 K for vairous diffusion times (see figure legend) measured for C_2H_6 [30], C_2H_4, CO_2, and CH_4 in ZIF-7-8 (empty, red symbols) and ZIF-8 (filled, black symbols). The solid lines for the ZIF-8 data represent a monoexponential fit (Eq. (1)) while the dashed red lines are the "effective" monoexponential fits based on the initial 30% of the signal attenuation in ZIF-7-8 and extrapolated to the signal attenuation values around 0.1. Crossed symbols correspond to the measurements at 17.6 T. All other symbols correspond to the measurements at 14 T. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Fig. 2. ^{13}C PFG NMR attenuation curves at low sorbate loadings (loading pressure above ZIF bed of 0.8 ± 0.08 bar) for vairous diffusion times (see figure legend) of ^{13}C labelled C_2H_6 [30], C_2H_4, CO_2, and CH_4 gas at 296 K in ZIF-7-8 (open symbols) and ZIF-8 (filled symbols). The solid lines for the ZIF-8 data represent a monoexponential fit (Eq. (1)) while the dashed red lines are the "effective" monoexponential fits based on the initial 30% of the signal attenuation in ZIF-7-8 and extrapolated to the signal attenuation values around 0.1. All data were measured on a 14 T spectrometer. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 1
Effective diffusivities and the corresponding ranges of root mean square displacement (RMSD) values measured by PFG NMR for pure gases in ZIF-7-8 at 296 K.

Material	Gas	Pressure above ZIF Bed (bar)	Concentration of Gas in ZIF (mmol/g)	$D_{eff} \times 10^{-11}$ (m^2s^{-1})	$D_{eff}c/p \times 10^{-11}$ (m^2s^{-1} mmol/(g bar))[a]	RMSD Range (μm)
ZIF-7-8	C_2H_6	7.9 ± 0.8	4.4 ± 1.1	0.64 ± 0.10	0.36	1.7 to 2.5
ZIF-7-8	C_2H_6	2.7 ± 0.3	2.9 ± 0.6	0.51 ± 0.08	0.56	1.3 to 2.2
ZIF-7-8	C_2H_6	0.78 ± 0.08	1.5 ± 0.3	0.36 ± 0.05	0.68	1.3 to 1.9
ZIF-7-8	C_2H_6	0.28 ± 0.03	1.1 ± 0.3	0.36 ± 0.05	1.4	1.3 to 1.9
ZIF-7-8	C_2H_4	8.1 ± 0.8	3.9 ± 0.8	3.5 ± 0.5	1.7	2.0 to 5.8
ZIF-7-8	C_2H_4	0.88 ± 0.13	0.88 ± 0.18	2.0 ± 0.3	2.0	1.5 to 4.4
ZIF-7-8	CO_2	7.6 ± 0.8	5.5 ± 1.1	9.1 ± 1.4	6.6	2.2 to 9.3
ZIF-7-8	CO_2	0.82 ± 0.12	0.48 ± 0.10	8.8 ± 1.3	5.1	2.2 to 6.5
ZIF-7-8	CH_4	7.6 ± 0.8	1.0 ± 0.2	4.2 ± 0.6	0.55	1.5 to 4.5
ZIF-7-8	CH_4	0.81 ± 0.12	0.15 ± 0.03	3.3 ± 0.5	0.60	1.3 to 4.0

[a] All $D_{eff}c/p$ values have an uncertainty of 40%.

part of the PFG NMR attenuation curves by Eq. (1) [37]. Table 1 shows such effective diffusivities in ZIF-7-8 that were obtained by fitting Eq. (1) to the attenuation data in Figs. 1 and 2 with amplitudes of Ψ between around 1.0 and 0.7. The slopes corresponding to the effective diffusivities are shown by red dashed lines in Figs. 1 and 2. Table 1 also shows the corresponding ranges of the root MSD values obtained using the Einstein relation (Eq. (2)) for the diffusion times used in the measurements. It was observed that in all cases these root MSD values were significantly smaller than the mean size of ZIF-7-8 crystals (~13 μm). Hence, any influence of the external crystal surface on the attenuation curves measured in ZIF-7-8 can be expected to be negligibly small [37]. This expectation is confirmed by the observed time independence of the effective diffusivities in ZIF-7-8 and by the coincidence of the corresponding attenuation curves for different diffusion times in the measured range (Figs. 1 and 2).

The results of fitting the attenuation curves for ZIF-8 in Figs. 1 and 2 using Eq. (1) at the smallest diffusion time along with the corresponding root MSD values are presented in Table S1. The smallest diffusion time data were used here and later to minimize any effects at the external crystal surface on the reported intra-ZIF diffusivities. Indeed, it is seen in Figs. 1 and 2 that for the smaller sorbates exhibiting faster diffusion in ZIF-8 there is some weak dependence of the

attenuation curves on diffusion time. Such dependence is attributed to the contribution of the effects at the external crystal surface because for faster diffusing sorbates root MSD values become comparable with the average size of ZIF-8 crystals (~18 μm). It was verified that the intracrystalline diffusivities measured for ZIF-8 in this work (Table S1) are in agreement, within uncertainty, with the previously published self-diffusivities measured by PFG NMR under the same or similar conditions [12,19,20]. Fig. 3 presents the ratios of the corresponding diffusivities in ZIF-8 and ZIF-7-8. It is seen in the figure that for each sorbate and loading pressure studied the self-diffusivity in ZIF-7-8 is much lower than that in ZIF-8, which is consistent with previously published permeation measurements [24]. The data in this figure will be discussed in more detail later.

In addition to diffusion of pure gases discussed above, diffusion of the following two-component gas mixtures was investigated in ZIF-7-8 by ^{13}C PFG NMR: C_2H_4/C_2H_6, CO_2/CH_4 and CO_2/C_2H_6. The sorbate loadings corresponded to sorption equilibrium at the total loading pressure of around 8 bar at 296 ± 1 K and equal or similar partial pressures of each sorbate. Figs S5, S6 and S7 present the PFG NMR attenuation curves for the mixed gas samples. Table 2 shows the effective diffusivities of each sorbate in the two-component mixtures. These diffusivities were obtained from the initial slopes of the
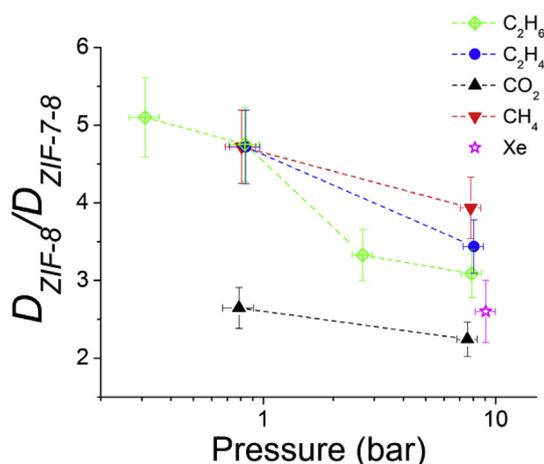
Fig. 3. Ratios of the sorbate self-diffusivities (D) in ZIF-8 to the effective self-diffusivities (D_{eff}) in ZIF-7-8 for C_2H_6, C_2H_4, CO_2, CH_4, and Xe at multiple sorbate loading pressures at 296 K.

attenuation curves as discussed above for the pure gases. Also shown in the table are the ranges of root MSD values calculated using Eq. (2).

The diffusion data in Tables 1 and 2 suggest that the diffusivity inside ZIF-7-8 crystals tends to increase with increasing total sorbate loading, especially when larger molecules like C_2H_6 (4.4 Å) [38,39] or C_2H_4 (4.2 Å) [38,39] are present in the sample. In particular, it was observed that the diffusivity of CO_2 in ZIF-7-8 is larger by a factor of around 1.4 when the sample is equilibrated with the CO_2/C_2H_6 mixture instead of pure CO_2 at a similar total loading pressure around 8 bar. For ZIF-7-8 loaded with pure ethane or ethylene the diffusivity is significantly larger when the loading pressure of the corresponding gas is larger. At the same time, for ZIF-7-8 loaded with pure CO_2 (3.3 Å) [39], the diffusivity is similar in the samples equilibrated with around 0.7 and 8 bar of CO_2. Diffusivity increase with increasing sorbate loading was also previously reported for ZIF-8 [16–19], and attributed mostly to the framework flexibility of ZIF-8.

It is important to note that, according to the transition state theory (TST) applied in its simplest form to the process of a molecular passage through narrow apertures separating adjacent pores, the self-diffusivity in microporous solids is expected to be proportional to the ratio of the sorbate pressure in the gas phase surrounding microporous particles (p) and the intra-particle sorbate concentration (c) [40]. In a recent study, the concentration dependence of the corrected diffusivity of several gases in ZIF-8 was successfully explained by this simple approach [41]. In order to evaluate the applicability of this approach to the observed concentration dependence of the self-diffusivity in ZIF-7-8, the values of $D_{eff}c/p$ were calculated and presented in Tables 1 and 2 for the pure and mixed gases. According to the TST approach, such values for a particular sorbate should be concentration independent, even in the case of mixed gas samples [42]. The data in the tables indicate that within a large experimental uncertainty of these values (40%) they are the same for each particular gas at different loading pressures, for the exception of ethane at the highest loading pressures. In this case, the TST approach overpredicts the self-diffusivity increase with an increasing ethane loading. This can be explained by additional factors such as framework flexibility related effects or molecular crowding effects, which are not taken into account by the simple TST approach discussed above. Qualitatively the same conclusion can also be made for the gas self-diffusion in the reference ZIF-8 material based on the comparison of the Dc/p values in Table S1 for the same gas type. Hence, the diffusivity increase with increasing loading pressure observed in the current work can be explained using the TST approach.

Most remarkably, the data in Fig. 3 show that for the sorbates larger than CO_2 at any given loading pressure used for the measurements of more than a single sorbate type there is no increase in the diffusivity

Table 2
Effective diffusivities and the corresponding ranges of root mean square displacement (RMSD) values measured by PFG NMR for gas mixtures in ZIF-7-8 at 296 K.

Mixed Gas Samples in ZIF-7-8	Total Pressure Above Particle Bed (bar)	Partial Pressure Above Particle Bed (bar)	Total Concentration (mmol/g)	Partial Concentration (mmol/g)	$D_{eff} \times 10^{-11}$ (m^2s^{-1})	$D_{eff}c/p \times 10^{-11}$ (m^2s^{-1} mmol/g bar))[a]	RMSD range (µm)
Ethane (C_2H_6/C_2H_4 mix)	8.2 ± 0.8	4.2 ± 0.4	3.2 ± 0.7	1.6 ± 0.3	0.71 ± 0.11	0.27	1.3 to 2.6
Ethylene (C_2H_6/C_2H_4 mix)	8.2 ± 0.8	4.1 ± 0.4	3.2 ± 0.7	1.6 ± 0.3	3.7 ± 0.6	1.4	1.4 to 5.9
CO_2 (CO_2/CH_4 mix)	7.7 ± 0.8	3.9 ± 0.4	3.5 ± 0.7	2.9 ± 0.6	9.0 ± 1.4	6.8	2.2 to 6.5
CH_4 (CO_2/CH_4 mix)	7.7 ± 0.8	3.8 ± 0.4	3.5 ± 0.7	0.60 ± 0.12	4.3 ± 0.6	0.68	1.5 to 4.5
CO_2 (CO_2/C_2H_6 mix)	8.6 ± 0.9	4.5 ± 0.5	3.6 ± 0.7	1.8 ± 0.4	13 ± 2	5.3	2.8 to 7.9
Ethane (CO_2/C_2H_6 mix)	8.6 ± 0.9	4.2 ± 0.4	3.6 ± 0.7	1.8 ± 0.4	0.61 ± 0.09	0.26	1.2 to 2.4

[a] All $D_{eff}c/p$ values have an uncertainty of 40%. c and p represent partial concentration and partial pressure in the mixed gas sample.

Table 3
Single component and mixed gas effective diffusion selectivities in ZIF-7-8 and single component diffusion selectivities in ZIF-8 at 296 K.

Material	Loading Pressure (bar)	Single Component or Mixed Gas	CO_2/CH_4 Diffusion Selectivity	C_2H_4/C_2H_6 Diffusion Selectivity
ZIF-8	8	Single	1.2 ± 0.1	6.0 ± 0.6
ZIF-8	0.8	Single	1.5 ± 0.2	5.5 ± 0.6
ZIF-7-8	8	Single	2.2 ± 0.2	5.4 ± 0.5
ZIF-7-8	0.8	Single	2.7 ± 0.3	5.5 ± 0.6
ZIF-7-8	8	Mixed	2.1 ± 0.2	5.2 ± 0.5

ratio in ZIF-8 and ZIF-7-8 with increasing size of gas molecules. Such an increase is expected for rigid apertures, which are smaller for ZIF-7-8 than for ZIF-8. Furthermore, complementary measurements of Xe diffusion in both ZIFs using ^{129}Xe PFG NMR (Fig. S8 and Table S3) show that for the large loading pressure around 8 bar the diffusivity ratio for Xe is comparable with that for CO_2, despite the fact that the kinetic dimeter of CO_2 is much smaller than that of Xe (~4.1 Å) [39,43]. All these observations suggest a larger influence of the framework flexibility on diffusion in ZIF-7-8 than in ZIF-8, especially for larger sorbates (C_2H_6, C_2H_4, and Xe).

Further indication of an increased influence of the framework flexibility on diffusion in ZIF-7-8 relative to ZIF-8 can be seen in Table 3. This table shows diffusion selectivities, which are defined as the ratios of the diffusivities of single sorbates in a mixture or the corresponding ratios for pure gases in the same porous material: $S_{a/b} = D_a/D_b$. For each material, diffusion selectivities remain the same within uncertainty between high and low loadings for both sets of gases being compared. It is seen that for the smaller sorbates (CO_2 and CH_4) the diffusion selectivity is larger in ZIF-7-8 than in ZIF-8, which is consistent with slower diffusion and expected smaller aperture sizes in the former ZIF in comparison with the latter. At the same time, for the larger sorbates (C_2H_4 and C_2H_6) the diffusion selectivity is similar in both ZIFs. Clearly, a higher extent of the framework flexibility in ZIF-7-8 in comparison to ZIF-8 can explain our results. This explanation is consistent with the computational results by Krokadis et al. indicating that ZIF-7-8 framework is more flexible than ZIF-8 though its effective aperture size is smaller [44]. In general, linker segmental dynamics is dominated by the flip-flopping motion of the linker in ZIF-8 as demonstrated by ^{2}H NMR [45].

4. Conclusions

A multinuclear PFG NMR technique was used to study microscale transport properties of a mixed-linker ZIF, ZIF-7-8, using multiple pure and mixed gases as probe molecules. The PFG NMR data reported here for ZIF-7-8 exhibits evidence of a distribution of diffusivities between ZIF-7-8 crystals in the studied sample, in agreement with the previously reported observation of such distribution for ethane diffusion using PFG NMR in combination with single-crystal IR microscopy. For each studied gas the effective (average) diffusivity in ZIF-7-8 was compared with the corresponding diffusivity in its parent material, ZIF-8. In all cases the measured self-diffusivities were found to be significantly lower in ZIF-7-8 than in ZIF-8. ZIF-7-8 was found to exhibit improved diffusion selectivity compared to ZIF-8 for CO_2/CH_4. It was attributed to the better sieving caused by the expected smaller pore aperture size in ZIF-7-8 than in ZIF-8. At the same time, similar diffusion selectivities were observed in both ZIFs for larger molecules (C_2H_4/C_2H_6). This observation was explained by framework flexibility effects, which manifest themselves in a distortion/increase of pore apertures when large sorbates are present inside ZIF-7-8. Although framework flexibility effects are also expected in the parent ZIF-8 material, these effects are more pronounced in ZIF-7-8, as demonstrated by the comparison of the diffusivity values and diffusion selectivities in both ZIFs

for different sorbate types and sorbate loadings.

Conflicts of interest

The authors have no competing interests to declare.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.micromeso.2019.109603.

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