Microscopic diffusion of pure and mixed methane and carbon dioxide in ZIF-11 by high field diffusion NMR

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Abstract

Multinuclear pulsed field gradient (PFG) NMR was used to study the self-diffusion of carbon dioxide and methane as equimolar mixtures and pure gases inside ZIF-11 crystals. Diffusion measurements were performed under conditions where the length scales of displacements were comparable with or smaller than the mean size of ZIF-11 crystals. It was found for both carbon dioxide and methane that the intracrystalline diffusivity decreases with an increasing diffusion time. Quantitative analysis of these time dependencies using a previously reported model explained the dependencies by the reflections of gas molecules from the external crystal surface. This analysis also allowed the intracrystalline gas diffusivities that are not perturbed by the influence of the external crystal surface to be determined. The ratio of such true intracrystalline diffusivities for CO₂ and CH₄ is found to be greater in the mixed sorbate sample than in the single-sorbate samples when the total gas concentration in each sample was the same within experimental error.

Keywords: Diffusion, PFG NMR, ZIF, MOF

1. Introduction

Zeolitic imidazole frameworks (ZIFs), a subclass of metal organic frameworks, have shown promising performance in challenging gas separations [1-8]. Specifically, the high surface area and pore volume, along with great chemical and thermal stability and control over the pore sizes, have already made ZIFs an excellent material choice for both adsorption- and diffusion-based separations. The tunable ZIF pore aperture, which is in the range of about 0.2 – 2 nm, can result in molecular sieving phenomena, allowing for high diffusion-based selectivity [2-4, 9].

Fundamental understanding of gas diffusion in ZIFs is of crucial importance for their potential applications in separations. Many diffusion studies of gases, including both molecular simulations and experimental research, have already been performed on ZIF-8 (for example, see references [4-6, 10-18]). Some of these studies were performed with pure ZIF-8 [6, 13-15, 17, 18], while others combined ZIF-8 with a polymer to form a mixed matrix membrane [5, 7, 12, 16]. Having comparable chemical and thermal stability with the same metallic center as ZIF-8, ZIF-11 is another interesting candidate for separations of small gas molecules. ZIF-11 consists of benzimidazole ligands and Zn^{2+} nodes arranged in a RHO topology, and is a polymorph of the more commonly studied ZIF-7 (SOD) structure. ZIF-7 is typically synthesized in N,N-dimethylformamide, while ZIF-11 has been shown to form in small alcohols with the addition of toluene, which serves as a structure directing agent via arene-arene interactions [19]. The smaller aperture size of ZIF-11 (3.0 Å) [3, 20] in comparison to that of ZIF-8 (3.4 Å) makes ZIF-11 an even more attractive choice for such separations. However, until now, there have only been a handful of studies of gas diffusion in ZIF-11, most involving molecular simulations [21-23]. To our knowledge, no measurements of microscopic diffusion have been reported for this material. Predicting diffusivities of guest molecules in ZIFs based on the pore and aperture sizes is a

challenging task because it is known that ZIFs exhibit significant framework flexibility. This framework flexibility may allow molecules with collision diameters larger than the aperture size to enter and diffuse in ZIF micropores. In particular, CH₄ molecules with the collision diameter around 3.8 Å can easily diffuse in ZIF-8 despite its aperture size of only 3.4 Å [17, 18].

Here we present microscopic studies of diffusion of CO₂, CH₄, and CO₂/CH₄ mixtures in ZIF-11. CO₂ and CH₄ are commonly found in natural gas and coal-bed streams where CO₂ is regarded as an impurity [24-26]. Both types of molecules were found to be able to enter and diffuse inside ZIF-11 crystals despite the ZIF-11 aperture size of 3.0 Å. As discussed above, this observation can be attributed to the framework flexibility of ZIF-11. Diffusion measurements were performed using ¹H and ¹³C pulsed field gradient (PFG) NMR utilizing a high field (17.6 T or 14 T) and high magnetic field gradients (up to 20 T/m) to obtain diffusivities for the length scales of displacements in the range of about 1-20 μm. These diffusion data determined the influence of the external crystal surface on the measured diffusivities, allowing the true intracrystalline diffusivities that are not perturbed by any effects at the external crystal surface to be examined. The diffusivities for single sorbates are compared with those for the corresponding gas mixtures. This comparison provides insights on the mutual influence of different sorbate components in ZIF-11 on the intracrystalline diffusion process.

2. Experimental

2.1. Materials and standard characterization

The synthesis of ZIF-11 was adapted from previously published work [3, 19]. Briefly, 0.6 g of benzimidazole (Alfa Aesar, 99%) was dissolved in 16.7 g of methanol (ACS Grade, VWR) and 3.7 g of NH₄OH (Sigma Aldrich, 28-30% NH₃ in water) in a 50 mL round-bottom flask. To

this, a solution of 0.6 g of Zn Acetate (Alfa Aesar, 97%) in 16.7 g of methanol and 13 g of toluene was added. The sample was stirred until mixed then allowed to stand for 4 h. White crystals were filtered through 22 μm filter paper and washed with methanol then dried under vacuum at 353 K overnight. Crystal size distribution was determined from scanning electron microscopy imaging (SEM, Hitachi SU8230 Cold Field Emission Scanning Electron Microscope) and processed using ImageJ processing software. The SEM image and the resulting crystal size distribution can be seen in Figs. 1 and S1, respectively. The mean crystal size of 30 ± 2 μm was obtained from the crystal size distribution in Fig. S1. It corresponds to the effective crystal radius of 15 ± 1 μm .

Figure 1

XRD patterns were collected on a Panalytical XPert PRO Alpha-1 X-Ray Diffractometer using a rotating sample stage on a zero-background slide. These patterns confirmed the ZIF-11 structure (Fig. 2). Major peaks of ZIF-11 are distinctly present and several notable peaks characteristic of ZIF-7 are not, indicating the successful synthesis of only one material phase. Differences in peak intensities are attributable to growth of particular crystal facets. The slight 2θ offset seen in the pattern is likely a combination of unit-specific calibration and refinement discrepancies.

Figure 2

2.2 NMR sample preparation

ZIF-11 crystals were placed inside a 5 mm (medium wall) NMR tube (Wilmad Labglass, Inc.). The height of the crystal bed inside the tube was equal to 25 ± 5 mm. The sample was activated by attaching the tube containing ZIF-11 to a custom-made vacuum system and heating the tube under vacuum to 423 K at a rate of 0.5 K/min to remove any sorbates present in the sample. Once the sample had been activated for 12 hours at 423 K, it was left to cool under high vacuum and room temperature conditions before sorbate loading was performed. Sorbates selected for this study were ^{13}C -enriched carbon dioxide (CO_2) and methane (CH_4), both consisting of a 99% isotopic purity (Sigma-Aldrich). Pure CO_2 and CH_4 as well as CO_2/CH_4 mixtures were loaded into the samples by cryogenically condensing the desired amounts into the NMR tube using liquid nitrogen. Upon loading, the NMR tube was flame sealed and separated from the vacuum system. NMR measurements were performed at least 3 hours after the sample preparation. During this period of time all samples were kept at room temperature to reach the sorption equilibrium at this temperature.

The gas concentrations in the ZIF-11 samples were determined by comparing the NMR signal of the adsorbed gas in these samples with the NMR signal of their bulk gaseous counterparts at a known pressure as discussed in Ref. [27]. Table 1 shows the gas concentrations in all ZIF-11 samples studied in this work.

Table 1

2.3 NMR Measurements

PFG NMR diffusion measurements were performed using a 17.6 T Avance III HD spectrometer (Bruker Biospin) and 14 T Avance III spectrometer (Bruker Biospin) operating at resonance frequencies of 750 MHz and 600 MHz for ^1H , respectively, and 188.6 MHz and 149.8 MHz for ^{13}C , respectively. Sine-shaped, bipolar magnetic field gradients with the effective duration of 1.5 ms and amplitudes up to 20 T/m were generated using Diff50 or Diff30 diffusion probes (Bruker BioSpin). The reported NMR data were obtained after keeping the samples at 296 K inside the magnet for at least one hour to ensure the sorption equilibrium conditions in the sample. This one hour equilibration was performed in addition to at least 3 hour equilibration at an essentially the same temperature outside the magnet. It was verified that the measured NMR data do not depend on the time in the magnet after the initial equilibration. In particular, the NMR signal, which is proportional to the total number of sorbate molecules in the ZIF-11 crystal bed, was monitored during the measurements that lasted several days at 296 K. There were no changes in the signal indicating no change in the gas concentration inside the bed. Hence, all reported NMR data correspond to the condition of sorption equilibrium at 296 K. Diffusion measurements were performed using the 13-interval PFG NMR pulse sequence with bipolar gradients [28], modified by the addition of a longitudinal eddy current delay. The diffusivities were obtained from the measured PFG NMR attenuation curves, i.e., dependencies of the PFG NMR signal intensity on the effective magnetic field gradient strength (g) with all other pulse sequence parameters held fixed. PFG NMR signal intensities were obtained separately for carbon dioxide and methane by integration of the corresponding NMR spectra. Under our measurement conditions, the ^{13}C NMR spectra of CO_2 and CH_4 consisted of single, non-overlapping lines at around 125 and -6.9 ppm, respectively (Fig. S2). The ^1H NMR spectrum of CH_4 consisted of a

single line at around 0.17 ppm. In the case of normal self-diffusion with a single diffusion coefficient (D), PFG NMR attenuation curves can be presented as [29]

$$\Psi = \frac{S(g)}{S(g \approx 0)} = \exp(-Dq^2t) \quad (1)$$

where Ψ is the PFG NMR signal attenuation, S is the PFG NMR signal intensity, t is the time of observation of diffusion process (i.e., diffusion time) and $q = 2\gamma g\delta$, where γ is the gyromagnetic ratio and δ is the effective gradient pulse length. In the case of normal self-diffusion in three dimensions, the mean square displacement (MSD) is related to D and t by the Einstein relation

$$\langle r^2 \rangle = 6Dt. \quad (2)$$

Longitudinal (T_1) and transverse (T_2) NMR relaxation times were estimated using the 13-interval PFG NMR sequence. For T_1 relaxation times, the measurements were performed by changing the time interval between the second and third $\pi/2$ radiofrequency pulses of the sequence while keeping all other time intervals constant. For T_2 relaxation times, the measurements were performed by changing the time interval between the first and second $\pi/2$ radiofrequency pulses of the sequence while keeping all other time intervals constant. Under the conditions of these measurements, it was ensured that there was no attenuation of the signal due to sorbate diffusion inside ZIF-11 crystals. At the same time, all signal from the gas phase of the sample was completely suppressed by the applied gradients. As a result, the reported T_1 and T_2 relaxation times correspond to carbon dioxide and methane located inside ZIF-11 crystals.

3. Results and Discussion

Under our measurement conditions, T_1 and T_2 NMR relaxation data were consistent with the absence of any distribution of relaxation times for both carbon dioxide and methane adsorbed

in ZIF-11 for all studied single component and mixture samples. Hence, a single T_1 and single T_2 NMR relaxation time was obtained for each sorbate, sample, and nuclei type. The NMR relaxation times are reported in Table 2.

Table 2

Fig. 3 shows examples of the measured ^1H and ^{13}C PFG NMR attenuation curves for CO_2 and CH_4 as both pure gases and gas mixtures diffusing in ZIF-11 crystals for diffusion times between 12 and 500 ms. Longer diffusion times were limited by the T_1 relaxation times. The majority of the diffusion measurements for both gases were performed by ^{13}C PFG NMR at 17.6 T. To confirm the absence of magnetic susceptibility effects and/or any other measurement artifacts under our experimental conditions, additional diffusion measurements were performed using ^1H PFG NMR (for methane) and ^{13}C PFG NMR (for methane and carbon dioxide) at a lower field of 14 T. Fig. 3 B shows that the ^1H and ^{13}C attenuation curves measured at 14 T coincide, within experimental uncertainty, with the corresponding ^{13}C attenuation curves measured in the same samples and for the same diffusion times at 17.6 T. This confirms the absence of any measurement artifacts under our experimental conditions.

The ^{13}C and ^1H PFG NMR attenuation curves seen in Fig. 3 have monoexponential behavior (i.e., linear in the semi-logarithmic presentation of the figure) with respect to q^2 in agreement with Eq. 1. This observation indicates that, for any particular sample and diffusion time, there is a single diffusivity for each studied sorbate (CO_2 and CH_4). These diffusivities are assigned to diffusion inside the crystals of ZIF-11 because the signal originated from molecules that diffuse in the gas phase of the sample for at least a fraction of diffusion time was attenuated away already at the smallest gradient strength used in the measurements. For each sorbate and

sample, the attenuation curves in Fig. 3 measured for different diffusion times have to coincide (see Eq. 1) if the diffusivity defined by the slope of the attenuation curve does not depend on diffusion time. The results in Fig. 3 indicate that the measured diffusivities of both sorbates are time-dependent because the slope of the attenuation curves decreases with increasing diffusion time. The best fit lines are shown in Fig. 3, with the corresponding diffusion data presented in Tables S1 and S2. Tables S1 and S2 also show the corresponding values of root MSD calculated using Eq. 2. These values were found to be smaller than or comparable with the average size of ZIF-11 crystals, supporting the observation of intracrystalline diffusion in our measurements.

Figure 3

The results in Tables S1 and S2 show that, for each sample, the diffusivity is decreasing with an increasing diffusion time. This dependence cannot be explained by the absence of sorption equilibrium in the samples under our measurement conditions because the NMR measurements discussed in section 2.3 demonstrate that all reported studies were performed after the sorption equilibrium was reached. NMR is an established technique for confirming or ruling out the condition of sorption equilibrium in beds of microporous particles [29]. The observed dependencies of the measured diffusivities on diffusion time can be attributed to the influence of the external crystal surface on diffusion process inside ZIF-11 crystals. Analytical relations describing such influence for diffusion in a range of sufficiently small diffusion times inside spherical crystals of radius R were introduced by Mitra et al. for the cases of the reflecting ($f = 4$) and adsorbing ($f = 2$) crystal surfaces [30-34]

$$\frac{D(t)}{D_0} \approx 1 - \frac{f}{3R} \left(\frac{D_0 t}{\pi} \right)^{\frac{1}{2}}, \quad (3)$$

where D_0 is the intracrystalline diffusivity in the limit of small times when any external surface effects can be neglected ($D_0 = D(t \rightarrow 0)$). In the case of the reflecting surface, a decrease of the intracrystalline diffusivity with increasing time is related to the expectation that an increasing fraction of diffusing molecules will encounter the external surface, which restricts the displacement growth because molecules cannot diffuse away from the crystals. Such reflections from the external surface can be a consequence of a much lower potential energy of these molecules inside the crystals than in the surrounding gas phase or due to a partial blockage of the external crystal surface resulting in the formation of transport barriers at the surface [29]. In the case of an adsorbing crystal surface, a decrease of the intracrystalline diffusivity with increasing time is related to the expectation that molecules with the largest displacements leave the crystals first. As a result, with increasing time, a growing fraction of these “fastest” molecules stop contributing to the ensemble used for calculating the intracrystalline diffusivity. This leads to decreasing intracrystalline diffusivity as a function of time. In this case, the NMR signal measured by the PFG NMR 13-interval sequence to determine the T_1 relaxation time (see Experimental section) should decrease with increasing time not only due to T_1 relaxation but also due to desorption of molecules from ZIF-11 crystals. The measurement data, however, did not show any evidence of such additional signal decrease. The absence of an additional signal decrease with increasing time is clearly consistent with the case of a reflecting surface in which molecules are prevented from leaving the crystals.

Fig.4 shows the normalized measured diffusivities D/D_0 plotted as a function of $(D_0 t)^{1/2}$ for all studied samples and sorbates. The solid line in Fig. 4 is the best fit line obtained by fitting all the data in the figure using Eq. 3 for the range of small times ($0.75 \leq D/D_0 \leq 1.0$) when Eq. 3 is expected to be valid. For $f = 4$ (reflecting surface) this line corresponds to the value of $R = 16$

$\pm 2 \mu\text{m}$, which is the same, within uncertainty, as the average radius obtained from the results of the SEM measurements. For $f = 2$ (adsorbing surface), the value of R corresponding to the best fit line is around 2 times smaller than that observed in SEM measurements. The fitting of the diffusion data using Eq. 3 was also performed separately for each sample and each sorbate type. The resulting best fit values of D_0 , which were used to normalize the diffusivities in Fig. 4, and the best fit values of R for $f = 4$ (reflecting surface) are presented in Table 3. The values of R in Table 3 for each sample and sorbate type were found to be the same, within uncertainty, as the value of R obtained from simultaneous fitting the data for all samples and sorbate types in Fig. 4. Based on all the results discussed above, we can conclude that the observed dependence of the measured intracrystalline diffusivity on time is mostly due to “reflections” of molecules from the external crystal surface at short diffusion times. As discussed above, such reflections can be a consequence of a much lower potential energy of sorbate molecules inside the ZIF crystals than in the surrounding gas phase. On the other hand, these reflections can occur due to a partial blockage of the external crystal surface resulting in the formation of transport barriers at the surface. It is important to note that at larger diffusion times sorbate molecules are expected to be able to permeate through the external crystal surface. This expectation is consistent with the lack of the transition from the $t^{1/2}$ to t^{-1} time scaling of (D/D_0) in Fig. 4 expected at large times for a fully reflective surface. It is important to note, however, that the observed distribution over the crystal sizes (Fig. S1) can make this transition to be a very gradual process.

Figure 4

Table 3

Table 3 shows the “true” intracrystalline diffusivities which are not perturbed by any affects at the external crystal surface. These diffusivities are shown in Fig. 5 as a function of the total sorbate concentration in a sample. It is seen that for both sorbates there is a trend of decreasing diffusivity with increasing total sorbate concentration in ZIF-11. A similar trend was observed previously in microporous materials [17, 29]. It can be explained by the expectation that the extent of mutual hindrance experienced by molecules in a diffusion process will increase with molecular concentration. The data in the figure shows that, for comparable total sorbate concentrations, the ratio of CO₂ and CH₄ diffusivities (viz. diffusion selectivity) in ZIF-11 loaded with a single gas is smaller than the corresponding ratio in ZIF-11 loaded with CO₂/CH₄ mixture. This observation has been seen in the results of infra-red microscopy measurements of effective transport diffusivities in ZIF-8 as well as in simulations performed for ZIF-8 and other microporous materials where the presence of CO₂ was observed to hinder the diffusion of CH₄ [17, 35-38]. For ZIF-8 this observation is explained by the preferred adsorption of CO₂ at the ZIF pore apertures, obstructing the pathways for CH₄ molecules to diffuse [17, 38]. To our knowledge, a larger ratio of CO₂ and CH₄ self-diffusivities for CO₂/CH₄ mixture than that for the corresponding single gases at the same total gas loadings has not been observed experimentally in MOFs until now.

Comparison of the single-component self-diffusivities in Table 3 and Fig 5 with the corresponding diffusivities reported for ZIF-8 in a similar loading range [18] indicates that the diffusivities of CO₂ and CH₄ are about 20-40% smaller in ZIF-11 than in ZIF-8. This observation is consistent with the discussed in the introduction aperture size, which is smaller in ZIF-11 than in ZIF-8. Clearly, self-diffusivities which are much smaller in ZIF-11 than in ZIF-8 can be expected for molecules larger than CO₂ and CH₄.

Figure 5

4. Conclusion

^{13}C PFG NMR at 17.6 T was utilized to study intracrystalline diffusion of mixed and pure CO_2 and CH_4 in ZIF-11. Additional diffusion measurements of the same ZIF-11 samples were also performed using ^1H and ^{13}C PFG NMR at 14 T. The coinciding diffusivities obtained for the same sorbate and under the same conditions when using different nuclei and field strength ruled out any measurement artifacts in the reported studies. Intracrystalline diffusivities of both CO_2 and CH_4 were found to decrease with increasing time of diffusion observation. Quantitative analysis of this time dependence concluded that it is due to reflections of diffusing molecules from the external crystal surface, which prevents molecules from desorbing from crystals on the millisecond time scale used in the measurements. Potential energy difference of the sorbate molecules located inside and outside the crystals as well as partial blockage of the external crystal surface were discussed as possible reasons for inability of CO_2 and CH_4 molecules to leave ZIF-11 crystals at short times used in the measurements. This analysis also allowed obtaining “true” intracrystalline diffusivities that are not perturbed by any surface effects. It was found that, for the same (within experimental error) total sorbate concentration in ZIF-11, the ratio of true CO_2 and CH_4 intracrystalline self-diffusivities in the mixed sorbate sample is greater than the corresponding ratio in the single-sorbate samples. The observed diffusion selectivity of around 4 for CO_2/CH_4 mixtures makes ZIF-11 an attractive candidate for membrane-based and pressure swing adsorption (PSA) separations of such mixtures. Our NMR data show that for the same partial pressure more CO_2 than CH_4 molecules are adsorbed in ZIF-11. Hence, the adsorption selectivity is expected to enhance the reported diffusion selectivity resulting in an

overall selectivity significantly larger than 4. This consideration justifies detailed studies of adsorption isotherms for CO₂/CH₄ mixtures in ZIF-11 in future studies.

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References

- [1] B.R. Pimentel, A. Parulkar, E.-k. Zhou, N.A. Brunelli, R.P. Lively, *ChemSusChem*, 7 (2014) 3202-3240.
- [2] J.A. Thompson, C.R. Blad, N.A. Brunelli, M.E. Lydon, R.P. Lively, C.W. Jones, S. Nair, *Chem. Mater.*, 24 (2012) 1930-1936.
- [3] J. Sánchez-Laínez, B. Zornoza, Á. Mayoral, Á. Berenguer-Murcia, Diego Cazorla-Amorós, C. Téllez, J. Coronas, *J. Mater. Chem. A*, 3 (2015) 6549-6556.
- [4] R. Mueller, S. Zhang, C. Zhang, R.P. Lively, S. Vasenkov, *J. Membr. Sci.*, 477 (2014) 123-130.
- [5] C. Zhang, Y. Dai, J.R. Johnson, O. Karvan, W.J. Koros, *J. Membr. Sci.*, 389 (2012) 34-42.
- [6] C. Zhang, R.P. Lively, K. Zhang, J.R. Johnson, O. Karvan, W.J. Koros, *J. Phys. Chem. Lett.*, 3 (2012) 2130-2134.

- [7] C. Zhang, W.J. Koros, J. Phys. Chem. Lett., 6 (2015) 3841-3849.
- [8] W. Li, Y. Zhang, Q. Li, G. Zhang, Chem. Eng. Sci., 135 (2015) 232-257.
- [9] T. Li, Y. Pan, K.-V. Peinemann, Z. Lai, J. Membr. Sci., 425-426 (2013) 235-242.
- [10] C. Chmelik, Microporous Mesoporous Mater., 216 (2015) 138-145.
- [11] M.V. Parkes, H. Demir, S.L. Teich-McGoldrick, D.S. Sholl, J.A. Greathouse, M.D. Allendorf, Microporous Mesoporous Mater., 194 (2014) 190-199.
- [12] R. Mueller, V. Hariharan, C. Zhang, R. Lively, S. Vasenkov, J. Membr. Sci., 499 (2016) 12-19.
- [13] E. Haldoupis, T. Watanabe, S. Nair, D.S. Sholl, Chemphyschem, 13 (2012) 3449-3452.
- [14] H. Bux, C. Chmelik, R. Krishna, J. Caro, J. Membr. Sci., 369 (2011) 284-289.
- [15] L. Hertäg, H. Bux, J. Caro, C. Chmelik, T. Remsungnen, M. Knauth, S. Frizsche, J. Membr. Sci., 377 (2011) 36-41.
- [16] M.J.C. Ordoñez, K.J.B. Jr., J.P. Ferraris, I.H. Musselman, J. Membr. Sci., 361 (2010) 28-37.
- [17] C. Chmelik, J. van Baten, R. Krishna, J. Membr. Sci., 397-398 (2012) 87-91.
- [18] A.-K. Pusch, T. Splith, L. Moschkowitz, S. Karmakar, R. Biniwale, M. Sant, G.B. Suffritti, P. Demontis, J. Cravillon, E. Pantatosaki, F. Stallmach, Adsorption, 18 (2012) 359-366.
- [19] M. He, J. Yao, Q. Liu, Z. Zhong, H. Wang, Dalton Trans., 42 (2013) 16608-16613.
- [20] K.S. Park, Z. Ni, A.P. Côté, J.Y. Choi, R. Huang, F.J. Uribe-Romo, H.K. Chae, M. O'Keeffe, O.M. Yaghi, Proc. Natl. Acad. Sci. USA, 103 (2006) 10186-10191.
- [21] W. Morris, N. He, K.G. Ray, P. Klonowski, H. Furukawa, I.N. Daniels, T.A. Houndonougbo, M. Asta, O.M. Yaghi, B.B. Laird, J. Phys. Chem. C, 116 (2012) 24084-24090.
- [22] G. Yilmaz, S. Keskin, Ind. Eng. Chem. Res., 51 (2012) 14218-14228.
- [23] P. Schierz, S. Frizsche, W. Janke, S. Hannongbua, O. Saengsawang, C. Chmelik, J. Kärger, Microporous Mesoporous Mater., 203 (2015) 132-138.
- [24] Y. He, Z. Zhang, S. Xiang, F.R. Fronczek, R. Krishna, B. Chen, Chem. Eur. J., 18 (2011) 613-619.

- [25] M.J. da Silva, Fuel Process. Technol., 145 (2016) 42-61.
- [26] Q. Yang, A.D. Wiersum, H. Jobic, V. Guillermin, C. Serre, P.L. Llewellyn, G. Maurin, J. Phys. Chem. C, 115 (2011) 13768-13774.
- [27] M. Dvoyashkin, J. Zang, G.I. Yucelen, A. Katihar, S. Nair, D.S. Sholl, C.R. Bowers, S. Vasenkov, J. Phys. Chem. C, 116 (2012) 21350-21355.
- [28] R.M. Cotts, M.J.R. Hoch, T. Sun, J.T. Markert, J. Magn. Reson., 83 (1989) 252-266.
- [29] J. Kärger, D.M. Ruthven, D.N. Theodorou, Diffusion in Nanoporous Materials, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2012.
- [30] O. Geier, R.Q. Snurr, F. Stallmach, J. Kärger, J. Chem. Phys, 120 (2004) 367.
- [31] P.P. Mitra, P.N. Sen, L.M. Schwartz, Phys. Rev. B: Condens. Matter, 47 (1993) 8565-8574.
- [32] P.P. Mitra, P.N. Sen, Phys. Rev. B: Condens. Matter, 45 (1992) 143-156.
- [33] M. Krutyeva, X. Yang, S. Vasenkov, J. Kärger, J. Magn. Reson., 185 (2007) 300-307.
- [34] R. Valiullin, J. Kärger, Chapter 12 Confined Fluids: NMR Perspectives on Confinements and on Fluid Dynamics, In R. Valiullin (Ed.) Diffusion NMR of Confined Systems: Fluid Transport in Porous Solids and Heterogeneous Materials, The Royal Society of Chemistry 2017, pp. 390-434.
- [35] R. Krishna, J.M. van Baten, Chem. Eng. J., 133 (2007) 121-131.
- [36] R. Krishna, J.M. van Baten, Chem. Phys. Lett., 446 (2007) 344-349.
- [37] R. Krishna, J.M. van Baten, Sep. Purif. Technol., 61 (2008) 414-423.
- [38] L. Zhang, G. Wu, J. Jiang, J. Phys. Chem. C, 118 (2014) 8788-8794.

Tables

Table 1: Sorbate loadings (in mmol g⁻¹) obtained for the porous samples used in this work using NMR signal analysis.

Sample Type	CO ₂	CH ₄
Mixture 1	0.6 ± 0.1	0.6 ± 0.1
Mixture 2	1.0 ± 0.2	0.9 ± 0.2
Mixture 3	1.6 ± 0.2	1.6 ± 0.2
Single sorbate samples	2.2 ± 0.3	2.1 ± 0.3

Table 2. ¹H and ¹³C NMR relaxation times for carbon dioxide and methane adsorbed in ZIF-11.

Nuclei	Sample Type	Measured Sorbate	<i>T</i> ₁ , ms [*]	<i>T</i> ₂ , ms [*]
¹³ C	Single Sorbate CO ₂	CO ₂	592	4.3
¹³ C	Mixture 1	CO ₂	450	4.6
¹³ C	Mixture 2	CO ₂	477	4.7
¹³ C	Mixture 3	CO ₂	778	4.7
¹³ C	Single Sorbate CH ₄	CH ₄	456	7.4
¹³ C	Mixture 1	CH ₄	443	10.5
¹³ C	Mixture 2	CH ₄	376	7.4
¹ H	Mixture 2	CH ₄	316	3.0
¹³ C	Mixture 3	CH ₄	372	10.7

*The experimental uncertainty is around 10%.

Table 3. Intracrystalline diffusivities in the limit of small diffusion times (*D*₀) at 296 K and the effective radius of the ZIF-11 crystal obtained by fitting the PFG NMR data with Eq. 3 for each ZIF-11 sample.

Sample Type	<i>D</i> ₀ (CO ₂), 10 ⁻¹⁰ $\frac{m^2}{s}$	<i>R</i> (CO ₂), μm	<i>D</i> ₀ (CH ₄), 10 ⁻¹⁰ $\frac{m^2}{s}$	<i>R</i> (CH ₄), μm
Mixture 1	2.1 ± 0.2	18 ± 3	0.60 ± 0.06	17 ± 3
Mixture 2	2.1 ± 0.2	15 ± 2	0.53 ± 0.05	16 ± 2
Mixture 3	1.4 ± 0.1	15 ± 2	0.30 ± 0.03	16 ± 2
Single Sorbate CO ₂	1.4 ± 0.1	16 ± 2	-	-
Single Sorbate CH ₄	-	-	0.75 ± 0.07	16 ± 2

Figure captions

Figure 1. SEM image of the ZIF-11 sample used for diffusion studies.

Figure 2. Powder XRD patterns of the measured ZIF-11 sample (the upper pattern), simulated ZIF-11 (the middle pattern) [20], and the ZIF-11 polymorph, ZIF-7 (the lower pattern) [20].

Figure 3. Examples of the PFG NMR attenuation curves measured in ZIF-11 for the following sorbates and samples at 296 K: (A) for CO₂ in a single-sorbate sample, (B) for CH₄ in a single-sorbate sample, (C) for CO₂ in Mixture 2 sample and (D) for CH₄ in in Mixture 2 sample. Measurements were performed by ¹³C PFG NMR at 17.6 T (filled symbols) and 14 T (hollow symbols with a cross) as well as by ¹H PFG NMR at 14 T (hollow symbols). The solid lines represent the results of least-square fitting using Eq.1.

Figure 4. Normalized measured diffusivities $D(t)/D_0$ as a function of $(D_0t)^{1/2}$ for all studied ZIF-11 samples and sorbates at 296 K. The solid line is the best fit line obtained by fitting all the data using Eq. 3. It corresponds to $R = 16 \pm 2 \text{ } \mu\text{m}$ for $f = 4$ (reflecting surface) and $R = 8 \pm 1 \text{ } \mu\text{m}$ for $f = 2$ (adsorbing surface). Data were obtained by ¹³C PFG NMR at 17.6 T (hollow and filled symbols), as well as by ¹³C PFG NMR (hollow symbol with a cross) and ¹H PFG NMR (hollow symbol with a horizontal line) at 14 T.

Figure 5. Intracrystalline diffusivities of CO₂ (▲) and CH₄ (▼) at 296 K in the limit of small diffusion times plotted as a function of total concentration of CO₂ and CH₄ in ZIF-11 crystals. Hollow and filled symbols show data for the single sorbate and mixed sorbate samples, respectively.

Figures

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Single Sorbates

Mixture