


รายงานวิจัยฉบับสมบูรณ์

โครงการพัฒนาและออกแบบวัสดุโลหะอินทรีย์ชนิดเลียนแบบซีโอไลต์สำหรับการแยกก๊าซ

โดย ผู้ช่วยศาสตราจารย์ ดร. ตติยา โชคบุญเปี่ยม

2 พฤษภาคม 2560

สัญญาเลขที่ MRG5980073

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ภาควิชาเคมี คณะวิทยาศาสตร์ มหาวิทยาลัยรามคำแหง

สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัย

(ความเห็นในรายงานนี้เป็นของผู้วิจัย
สกว. และ สกอ. ไม่จำเป็นต้องเห็นด้วยเสมอไป)

บทคัดย่อ

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ระยะเวลาโครงการ: 1 ปี

เนื่องจากความต้องการเทคโนโลยีการแยกก๊าซที่เพิ่มสูงขึ้น, วัสดุรูพรุนโครงข่ายซีโอไลติกอิมิดาโซเลต (ซิฟ) เป็นวัสดุชนิดใหม่ที่มีศักยภาพสำหรับการแยกก๊าซ โดยวัสดุดังกล่าวมีพื้นที่ผิวขนาดใหญ่ สามารถปรับขนาดโครงสร้างหน้าต่าง ทนต่อความร้อนสูงและเสถียรต่อสารเคมี อย่างไรก็ตาม ยังขาดความรู้ด้านพฤติกรรมของก๊าซระหว่างการขนส่งผ่านเมมเบรนด้วยวัสดุชนิดนี้ ดังนั้นในงานวิจัยนี้ได้ตรวจสอบและศึกษาในระดับอะตอม เช่น การดูดซับก๊าซ และกระบวนการแพร่ของก๊าซที่น่าสนใจ (คาร์บอนไดออกไซด์, ไนโตรเจน, มีเทน, ไฮโดรเจน) และก๊าซผสม (คาร์บอนไดออกไซด์/ไนโตรเจน, มีเทน/ไฮโดรเจน) ภายในโครงสร้างซิฟแบบยืดหยุ่นโดยการจำลองแบบด้วยคอมพิวเตอร์ การจำลองแบบได้ถูกดำเนินการโดยโปรแกรม DL_POLY เวอร์ชั่น 2.20 สำหรับการจำลองพลวัตเชิงโมเลกุล (MD) และการจำลองกิบส์มอนติคาร์โล (GEMC) ผลที่ได้จากการคำนวณทำให้เกิดความเข้าใจต่อกลไกของการขนส่งก๊าซ ตำแหน่งการดูดซับก๊าซในโครงสร้างวัสดุ การดูดซับก๊าซ และประสิทธิภาพการแยกก๊าซผสม ความรู้ที่ได้จากงานวิจัยนี้สามารถนำมาใช้เพื่อพัฒนาหรือเพิ่มประสิทธิภาพของวัสดุซิฟในงานอุตสาหกรรมในอนาคตอันใกล้นี้

คำหลัก: การดูดซับ, การแยก, วัสดุโลหะอินทรีย์ชนิดเลียนแบบซีโอไลต์, การคำนวณทางคอมพิวเตอร์

Abstract

Project Code: MRG5980073

Project Title: Development and design of Zeolitic Imidazolate Frameworks for gas separation application

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Project Period: 1 year

With increasing demand in gas separation technologies, Zeolitic Imidazolate Frameworks (ZIFs) are emerging as potential materials for gas separation applications based on their large surface areas, adjustable window size and exceptional thermo and chemical stabilities. However, the lack of knowledge for gas behavior during gas transports through the membrane somewhat limited the applicability of these materials. Hence, in this work, we are going to examine and study in atomic scale the adsorption isotherm and diffusion process of some interesting gases (CO_2, N_2, CH_4, H_2) and their mixture (CO_2/N_2, CH_4/H_2) inside flexible ZIFs by computer simulations. The simulations are conducted by DL_POLY program version 2.20 for Molecular Dynamics (MD) simulation and Gibbs Ensemble Monte Carlo (GEMC) simulations. The results are expected to give a better understanding for mechanisms of gas transport, adsorption sites in the framework structure, adsorption isotherms and separation factors in gas mixtures. The knowledge obtained in this work can be used to improve or to enhance the ZIFs performance in many industrial applications in the near future.

Keywords: Adsorption, Separation, Zeolitic Imidazolate Frameworks, Computational Calculation

Executive Summary

1. Introduction to the research problem and its significance

For a long time, porous materials have received a lot of concern from scientists because of its applications in industry such as ion exchange, separation or catalysis. Zeolites play an important role as a typical porous material with an exceptional chemical and thermal stability; however, the difficulty of controlling the pore aperture is one of limitations of this material. Recently, a new class of porous materials has been synthesized, called Metal-Organic Frameworks (MOFs) which are also known as “hybrid organic inorganic frameworks”. Possessing higher surface area, larger pore volume and especially adjustable pore aperture, MOFs seem to be a good candidate for many industrial applications.

Especially, starting from 2006 Zeolitic Imidazolate Frameworks (ZIF’s) have been synthesized, being a subclass of MOFs but with zeolite like structures. They are composed of tetrahedral metal ions (Zn, Co…) with linkers that can be imidazolate (Im) or its derivatives. Because of this special structure, ZIFs have many advantages combining between traditional porous material (Zeolite) and new ones (MOFs). There are over 150 ZIF structures found by replacing the metal, linker or just the functional group in the linker. This rapid development of ZIF’s shows to some extent the importance of this new class of materials.

The rapid development in many industrial areas always leads to an increased pollution of the environment, thus, exhaust gas treatment is one of urgent issues that need to be solved. Among emission gases, CO_2 is known as a main green-house gas or the main reason for global warming. CO_2 enters the environment through burning fossil fuel like coal, oil or waste from chemical reactions. That’s the reason why separation of CO_2 from gas mixtures for treatment before emitting to the air or storage of CO_2 is necessary. While CO_2/H_2, CO_2/CH_4 mixtures can be easily separated by molecular sieving due to the different kinetic diameter, separation of CO_2/N_2 mixtures in post combustion process meet the difficulty of the similar size (CO_2 3.3Å and N_2 3.6Å).

On the other hand, hydrogen (H_2) is regarded as a future fuel or fuel cell which is clean, renewable and reduces the green house effect. To produce hydrogen for application, one of the most popular methods is steam reforming and methane (CH_4), well-known for being one of the impurities, needs to be removed or separated from hydrogen. That is also the reason why many researchers try to find materials having a high selectivity for CO_2/ N_2 and CH_4/H_2 mixtures. MOFs, or more specific ZIFs are emerging as promising candidates for these purposes.

Based on their interesting properties, there is no surprise that a lot of scientists study about potential of ZIFs materials in gas separation and gas storage. In addition to this, with the recent development of better computational tools, simulation can serve as a bridge between experiment and theory, it can explain the mechanisms inside many processes as experiment can't do. Understanding the intrinsic properties of ZIFs from computer simulations can be used to predict experiments, save a lot of money as well as time for testing and improving this material.

Because ZIF's are porous materials, the mechanism of gas transport through ZIF's membranes will take place by diffusion. Hence, adsorption and diffusion are the most important processes for studying how to apply ZIFs in reality. From literature review, the flexibility of many ZIFs have been proven by both experimental and computational results such as gate opening effect or the movement of large molecules through the membrane. While adsorption is not affected much by the flexibility of ZIFs, it's impact on self-diffusion of guest molecules inside ZIFs is strong. However, the effect of the choice of interaction parameters for rigid and flexible models on self-diffusivities (D_s) and the effect of the gas molecule concentration on the ZIF's structure are still questionable.

For the above reasons, in this work, we are going to simulate adsorption and diffusion processes in both Monte Carlo (MC) and Molecular Dynamics (MD) simulations of guest molecules (CO_2, N_2, CH_4, H_2) and their mixture (CO_2/N_2, CH_4/ H_2) in ZIFs. The effect of flexible frameworks, gas molecule concentrations to ZIF's structure as well as separation factors of mixtures will be studied. The results obtained hopefully can provide a better understanding on atomic level for many physical processes in ZIFs. Scientists can utilize that knowledge, for applications in experiment and industrial processes in the near future for these promising materials.

2. Objectives

Examining and studying the diffusion and adsorption of guest molecules and their mixture in ZIF-8 and ZIF-90 and obtaining better understanding about the mechanisms and guest behavior during these processes in molecular scale.

3. Methodology

3.1 Finding and studying background information from theory and literature review.

3.2 Building structure of ZIF-8 and ZIF-90 from the X-ray data on CCDC (Cambridge Crystallographic Data Centre), using 2x2x2 unit cells for the simulation box.

3.3 Using Gibbs Ensemble Monte Carlo (GEMC) simulations to obtain adsorption isotherms for guest molecules.

3.4 Preparing the input files for different loadings of guest molecules (CO_2, N_2, H_2, CH_4) in ZIF-8 and ZIF-90 with various concentrations: 8, 40, 80, 120, 160, 200, 240 molecules at 300 K and 1 atm in the simulation box. The MD simulations will be carried out by use of the DL-POLY 2.20 program. After that, the results are analyzed:

- Plot the graph for various Radial Distribution Functions (RDFs) and find the adsorption sites
- Analyze the window size for the six-member ring.
- Calculate the self-diffusion coefficient (D_s) at all concentrations. The simulation will be conducted on both rigid and flexible frameworks in NPT, NVT and NVE ensemble.

3.5 Examining gas mixtures (CO_2/ N_2, H_2/CH_4) with ratio 1:1 at 300 K and 1 atm, comparison with single gas results and calculation of the separation factor.

3.6 Comparing the results with the experimental data such as adsorption site, adsorption isotherm, self diffusion coefficient, permeability and selectivity

3.7 Drawing conclusions and writing the publications.

4. Research plan

Research Plan	1st year				2nd year			
Description	Month				Month			
	1-3	4-6	7-9	10-12	1-3	4-6	7-9	10-12
1. Reviewing literature, from X-ray data, building structure for simulation box	*							
2. Study 1 st system ZIFs with CO_2, N_2 and their mixture								
Preparing input file for simulations		*						
Running simulations with different concentration of guest molecules (8-240)								
Single gas : CO_2, N_2		*						
Mixture gas: CO_2/ N_2			*					
Analyzing results - Lattice constant, window size - RDF distribution for adsorption sites - Self-diffusion coefficient (Ds) with various concentration - Separation factor for mixture gas				*				
3. Study 2nd system ZIFs with CH_4, H_2 and their mixture								
Preparing input file for simulations					*			
Running simulations with different concentration of guest molecules (8-240)								
Single gas : CH_4, H_2					*			
Mixture gas: CH_4/ H_2						*		
Analyzing results - Lattice constant, window size - RDF distribution for adsorption sites - Self-diffusion coefficient (Ds) with various concentration - Separation factor for mixture gas							*	
4. Comparing the results with the experimental data and drawing conclusions				*			*	
5. Writing publications							*	*

5. Expected outputs in ISI

Title: Structural and dynamical properties of gases adsorbed on the Zeolitic Imidazolate Frameworks

Journal: Microporous and Mesoporous Materials

Impact factor: 3.453

6. Budget details

	1st	2nd	total
1. Remuneration - salary for principal investigator 24 months	156,000	156,000	312,000
2. Materials - office materials, paper, CD, and thump drive - upgrade computer	25,000 25,000	25,000 25,000	50,000 50,000
3. Operational costs - activity at Thailand research fund - conferences in Thailand (transportations and accommodations) - copy and print documents - report	5,000 24,000 10,000 5,000	5,000 24,000 10,000 5,000	10,000 48,000 20,000 10,000
4. wage - assistant researcher	50,000	50,000	100,000
total in this project			600,000

Assistant researcher

- Responsible the computer cluster such as maintenance, installing programs for computational calculations *i.e.* Linux, Fortran, Gaussian, DL_POLY and Material Studio.
- Preparing the structures, input files for Molecular dynamics simulation and Grand Monte Caro simulation.

Content of the research

1. Methane in Zeolitic Imidazolate Framework ZIF-90: Adsorption and Diffusion by Molecular Dynamics and Gibbs Ensemble Monte Carlo

(Accepted by Microporous and Mesoporous Material, 235 (2016), 69-77.)

In this part, structural property like radial distribution functions (RDF's) as well as adsorption and self-diffusion of methane molecules in ZIF-90 are examined by both Molecular Dynamics (MD) and Gibbs Ensemble Monte Carlo (GEMC) simulations. Studying diffusion and adsorption of methane in ZIF-90 shows the influence of the framework flexibility on these properties. In addition, a better understanding on the atomic level of the adsorption isotherm, diffusion mechanisms, or adsorption sites can be achieved. It is still much uncertainty about the choice of parameters to be used in such simulations. Therefore, in this work, various parameters for the ZIF-90 lattice and for methane molecules from the literature will be tested and compared for rigid and flexible models.

1.1 Gibbs Ensemble Monte Carlo (GEMC) simulations

The structure of the ZIF-90 framework was obtained from the Cambridge Crystallographic Data Centre (CCDC) [1].The most common force fields for the framework that could produce a stable lattice size and dynamical properties were that of GAFF (which is a generalized AMBER force field) [2] and that of DREIDING [2]. Therefore, GAFF and DREIDING as well as modifications of them were tested in this work to describe both the bonded and the non-bonded interactions. The charges of atoms of ZIF-90 and methane were shown in Table 1 and 2, respectively.

Table 1. Partial charges of the atoms in the ZIF-90 framework

Atom type	Charge (Gee et al. [2])	Adjusted charge
C_CR	0.2104	0.21
C_CC	-0.0001	-0.002
C_CT	0.2582	0.258
H_H4	0.1149	0.115
H_HT	0.0476	0.049
Zn	0.6726	0.674
O	-0.4091	-0.41
N	-0.332	-0.335
total charge of the lattice	1.728	0

Table 2. Force fields for methane

Source	Molecules	ε (K)	σ (Å)	Charge
FF1 [3]	CH_4	158.5	3.72	0
FF2 [4]	CH_4	147.9	3.73	0
FF3 [5]	CH_4	173.2	3.8842	0
FF4 [6]	CH_4	191.235	3.71	0
FF5 [7]	$C(CH_4)$	30.7	3.74	-0.24
	$H(CH_4)$	14.1	2.67	0.06

The temperature was chosen to be 303 K for a comparison with the experimental data of [8] for testing the force fields. The box size used in Gibbs Ensemble Monte Carlo (GEMC) simulations is 69.086 Å (4x4x4). The results are shown in Fig. 1.

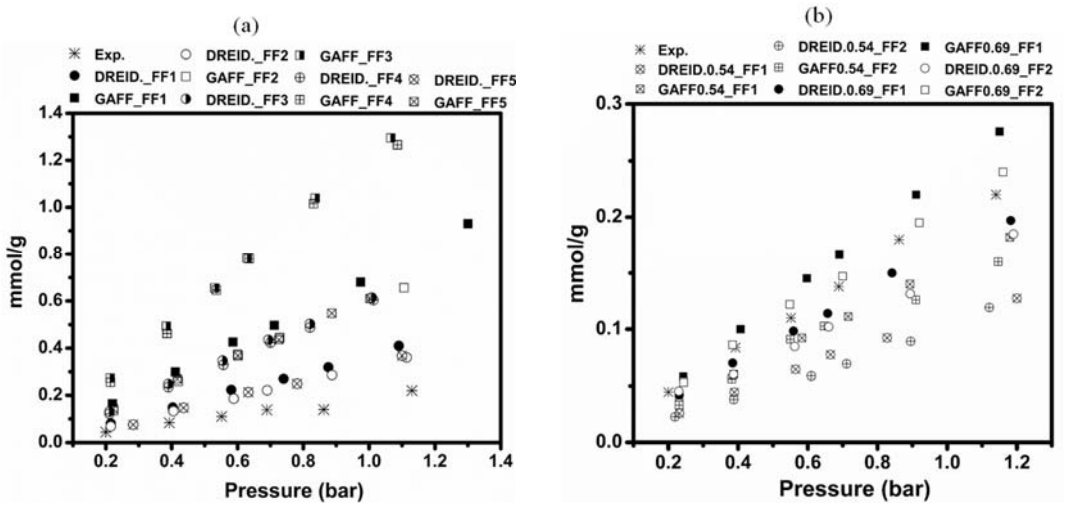

Fig. 1 a) Comparison of adsorption isotherms of five force fields for CH_4 (FF1-FF5) in ZIF-90 b) The adsorption isotherm of CH_4 in ZIF-90 after scaling the force field of the framework.

Fig. 1a shows that there is no force field which can produce the adsorption isotherm well. Hence, the well-depth was scaled by the scaling factor obtained from Pérez-Pellitero et al. [9] $\varepsilon^* = 0.69\varepsilon$, $\sigma^* = \sigma$ and Zhang et al [10] $\varepsilon^* = 0.54\varepsilon$, $\sigma^* = \sigma$ for both GAFF and DREIDING force fields. We call GAFF scaling 0.69 (GAFF 0.69), GAFF scaling 0.54 (GAFF 0.54), DREIDING scaling 0.69 (DREID. 0.69), DREIDING scaling 0.54 (DREID. 0.54). The scaling was used only two popular

force fields of guest molecules (FF1 and FF2) because these two force fields of methane have shown a good performance in many previous publications [3,4,9,11,12]. The adsorption isotherms obtained after modifying the force fields are shown in Fig. 1b.

It can be seen from Fig. 1b, that the modified GAFF (GAFF 0.69) and the modified DREIDING (DREID. 0.69) force fields can produce better results for adsorption isotherms when they were compared with the others. Therefore, GAFF 0.69 and DREID. 0.69 force fields were chosen to further study of the structure and dynamical properties.

1.2 Molecular Dynamics (MD) simulations

The force fields which gave good results for the adsorption isotherm were used to study also dynamical properties and the structure of ZIF-90 in MD simulations. The MD simulation was conducted flexible framework to compare the results and find out the importance of the structure flexibility of ZIF-90 for methane as guest. All MD simulations in this work were run by DL_POLY 2.20 [13].The MD simulation box was contained 2x2x2 unit cells (34.543Å). First, to control the temperature of the system, isochoric-isothermal ensemble (NVT) MD simulation was conducted for 5ns. After that, the system was allowed to equilibrate for 0.5 ns and then the dynamical properties were examined during 10 ns in the NVE ensemble. The window size distribution and the self-diffusion coefficient can be evaluated from the trajectories of these runs. Loadings of 0.5, 2.5, 10 and 15 CH_4 molecules/cage inside ZIF-90 were examined. The temperature was always 300K in the MD runs. The results were compared with available experiments and they were used to study adsorption sites and self-diffusion coefficients as well as the membrane permeance.

The distribution of window sizes in Fig. 2, it was confirmed again that the better structures were gained from GAFF and GAFF 0.69 force fields.

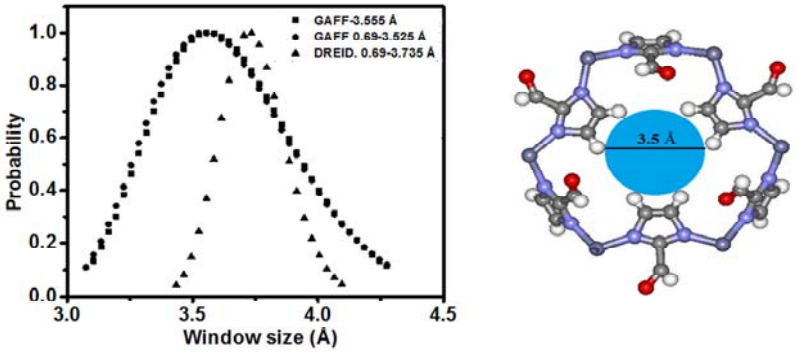

Fig. 2 Distribution of the fluctuating window size of the flexible ZIF-90 framework without guest molecules at 300K.

The window size in ZIF-90 from DREID 0.69 (3.735 Å) is quite larger than GAFF (3.555 Å), GAFF 0.69 (3.525 Å) and experiment (3.5 Å). It is concluded that the modified GAFF can produce not only the adsorption isotherms that fit to the experiment but can also keep the structural quantity such as window size. On the other hand, modified DREIDING just only gives adsorption isotherms in good agreement with the experiment.

The radial distribution functions (RDFs) between methane and selected atoms in the framework are plotted at very low (0.5 molecules/cage) loadings in MD simulation with modified GAFF force field as shown in Fig. 3.

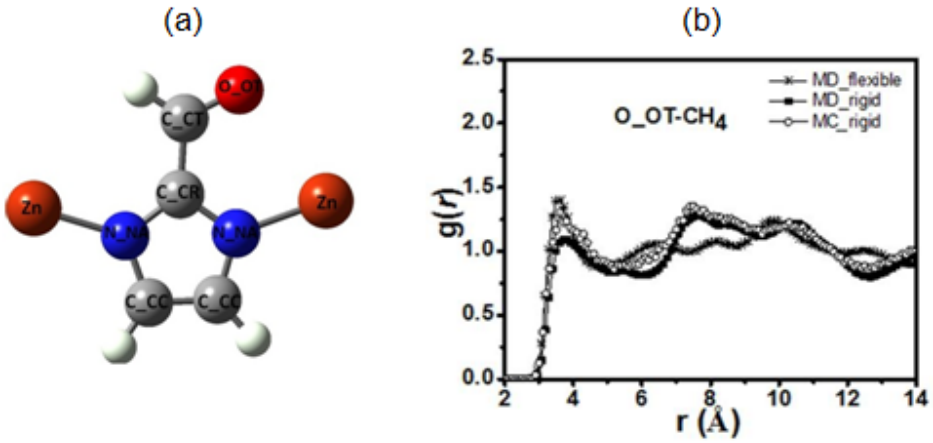

Fig. 3 a) Atom types in ZIF-90 b) RDF of the interaction between methane-ZIF-90 lattice rigid and flexible MD simulations at very low loading (0.5 CH_4 molecules/cage) with modified GAFF at 300 K.

At low loading (0.5 molecules/cage), the first RDF peak for O_OT-CH_4 was found to be shorter (3.6 Å) than another atom types in ZIF-90. Thus, at low loading, methane molecules are preferentially located at the organic linker. It is not surprising that O_OT is the most favorite site of methane based on the strong van der Waals interaction between O and CH_4.

The dynamical properties of guest molecules were examined by calculating their self-diffusion coefficient (D_s). The dynamical behavior of the lattice was investigated by the window size distribution. These results have been obtained in NVE ensemble MD as shown in Fig. 4.

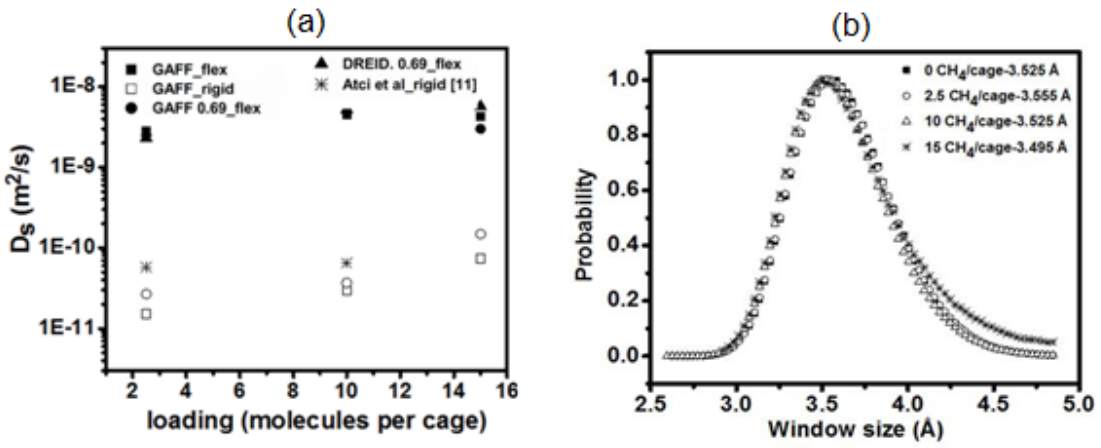

Fig. 4 a) Comparison of D_s for CH_4 in rigid and flexible ZIF-90 frameworks at 300K. b) Distributions of the window size of ZIF-90 for different loadings of CH_4 at 300 K.

The MD simulations were conducted on both rigid and flexible framework models. The D_s data are given in Fig. 4a and compared with the previous work of Atci et al. [11] who used a UFF rigid model for MD simulation. The D_s of methane was calculated to be zero in the DREID. 0.69 rigid model that means that no methane diffusion in ZIF-90 could be proven by this model. In Fig. 4a we can see the big gap of the D_s data between rigid and flexible framework. The methane can diffuse several orders of magnitude faster in the flexible model than in the rigid one. However results for D_s, from the flexible force fields, modified DREIDING, modified GAFF and original GAFF are similar. The larger window diameter of DREIDING obviously compensates the influence of the lower flexibility for methane in ZIF-90 for this force field. In Atci et al., the authors tried to compare their results with experimental permeation measurements. However, their predicted permeances for relative large molecules like methane, nitrogen were much lower than the experimental data. In [11] this was explained by the underestimation of D_s leading to a small permeance of these molecules. According to [11] the rigid framework was the reason. Therefore, to obtain more suitable D_s, a flexible model is necessary. From the adsorption isotherm and D_s at 200^0C and 1 bar with modified GAFF, the permeability was calculated by the below formula [12]. The permeance of methane through ZIF-90 obtained in this work is 3.5×10^{-8} ($mol.m^{-2}.s^{-1}.Pa^{-1}$). This is twice the experimental value of Huang et al. [14] which is 1.57×10^{-8} ($mol.m^{-2}.s^{-1}.Pa^{-1}$). Nevertheless, our value is nearer to the experiment than the value from rigid model in Atci et al. [11], which is 3×10^{-9} ($mol.m^{-2}.s^{-1}.Pa^{-1}$). The remaining difference could be explained by imperfect crystals in the real experiment while the crystal is considered ideal in the simulation.

For distributions of the window size at different loadings of methane in ZIF-90, the average window size of ZIF-90 was nearly unchanged. It increases from 3.525 Å to 3.555 Å at 2.5 CH_4/cage and decrease at very high loading from 3.555 Å to 3.495 Å (Fig. 4b). Throughout the observed range of density and hence pressure up to 255 bar, no discontinuous change of the window size appears. This indicates that no structural change like gate opening can be observed and the experimentally observed adsorption and permeation of “too big methane” molecules is explained by the framework flexibility of ZIF-90.

2. Importance of ZIF-90 Lattice Flexibility on Diffusion, Permeation and Lattice Structure for an adsorbed H_2/CH_4 Gas Mixture: A Re-Examination by Gibbs Ensemble Monte Carlo and Molecular Dynamics Simulations

(Accepted by Journal of Physical Chemistry C, 121 (19) 2017, 10455-10462.)

In this work, adsorption and diffusion for the 1:1 gas mixture H_2/CH_4 are studied. The results are compared with experimental data and other simulation work. In addition, the adsorption selectivities and the membrane separation factors are calculated and evaluated. Favorite adsorption sites are determined by the radial distribution functions (RDFs) and the probability densities. Furthermore, the diffusion coefficients (D_s) of the guest molecules CH_4 and H_2 inside ZIF-90 at different temperatures have been determined by Molecular Dynamics (MD) and Gibbs Ensemble Monte Carlo (GEMC) simulations. The size distribution of the window diameter has been checked at different temperatures and loadings in order to find a possible gate opening effect.

2.1 Gibbs Ensemble Monte Carlo (GEMC) simulations

Adsorption isotherms of CH_4, H_2 and the H_2/CH_4 mixture at 300 K obtained from GEMC simulations are collected in Fig. 5. The adsorption curves are linear. For comparison, in the case of methane in ZIF-90 it was found in [15] that the linear relationship is valid up to about 10 bar. The adsorbed amount of hydrogen is much smaller, far from filling the cavities, so that the linear law will be valid for hydrogen even up to higher pressure. This is confirmed by the adsorption isotherm in Fig. 5a.

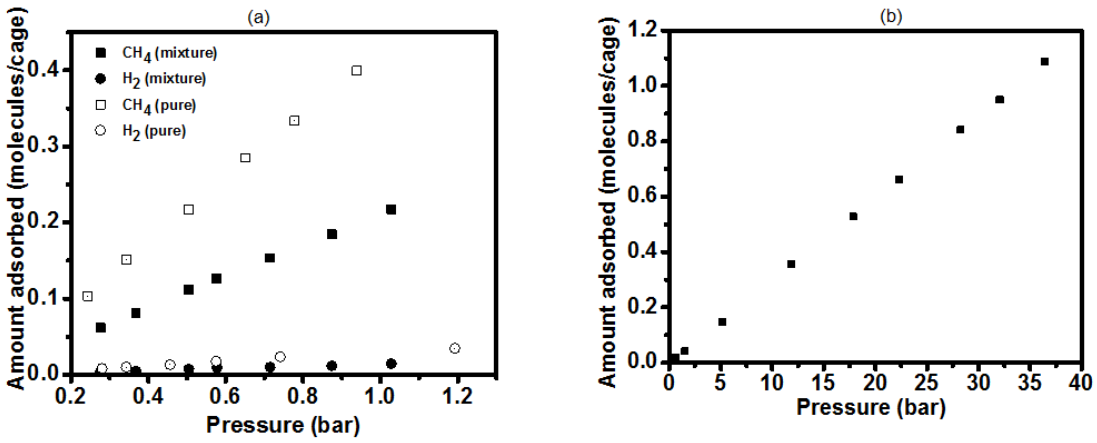

Fig. 5 a) Adsorption isotherms of the single components CH_4 and H_2 as well as of the equimolar H_2/CH_4 mixture in ZIF-90 at 300 K. b) Adsorption isotherm of pure H_2 at 300 K up to 40 bar.

The reason for the higher adsorbed amount of CH_4 in comparison with the smaller and lighter H_2 molecules is attributed to the stronger attraction between methane and the lattice atoms of ZIF-90. In addition, the adsorption of the H_2/CH_4 mixture was also evaluated at three different temperatures as shown in Fig. 6. As expected, the amounts adsorbed decrease with increasing temperature. This temperature dependence can be easily understood by applying the lowest term of the fugacity expansion which can be used for the linear part of the adsorption isotherm (like Henry's law) [16].

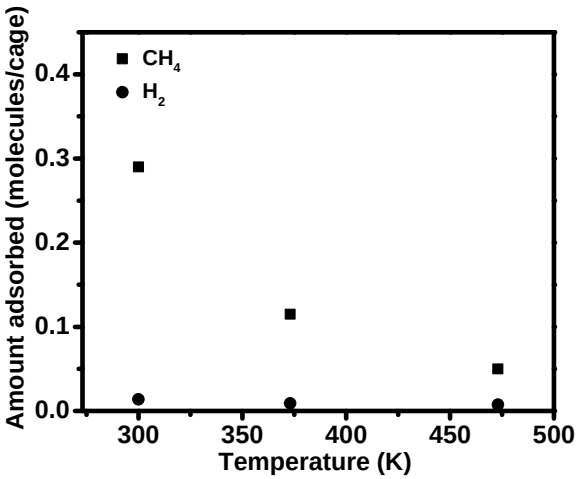

Fig. 6 Adsorbed amounts of CH_4 and H_2 as a function of temperature at 1 bar total pressure of the equimolar gas mixture H_2/CH_4.

The corresponding CH_4/H_2 adsorption selectivity for the equimolar mixture amounts 14.2 (0.07) at 300K, 7.1 (0.14) at 373K, and 3.6 (0.28) at 473K (data in brackets are the H_2/CH_4 selectivities).

Atci et al. [11] found at ambient temperature in GCMC simulations a CH_4/H_2 adsorption selectivity of around 15 what agrees very well with our data. This agreement can be expected because the approximation of a rigid lattice works well for the prediction of adsorption and we also do the GEMC with rigid lattice. The independence of the adsorption selectivity upon the pressure was also found in [11].

2.2 Molecular Dynamics (MD) simulations

2.2.1 The self-diffusion coefficient (D_s)

The self-diffusion coefficient D_s of the guest molecules has been calculated at 3 different temperatures corresponding to the experiment at 1 bar are shown in Fig. 7a. With the increase of temperature, D_s also increase. This is the usual temperature dependence of D_s according to the Arrhenius theory because of the higher thermal energy of the particles at higher temperatures. Furthermore, since the adsorption of methane decreases significantly, the fewer methane molecules in the ZIF framework have more space to move and this also leads to the higher D_s for both kinds, especially for H_2. This phenomenon had been mentioned in Huang et al. [17] when they conducted permeation experiments at these three temperatures at 1 bar.

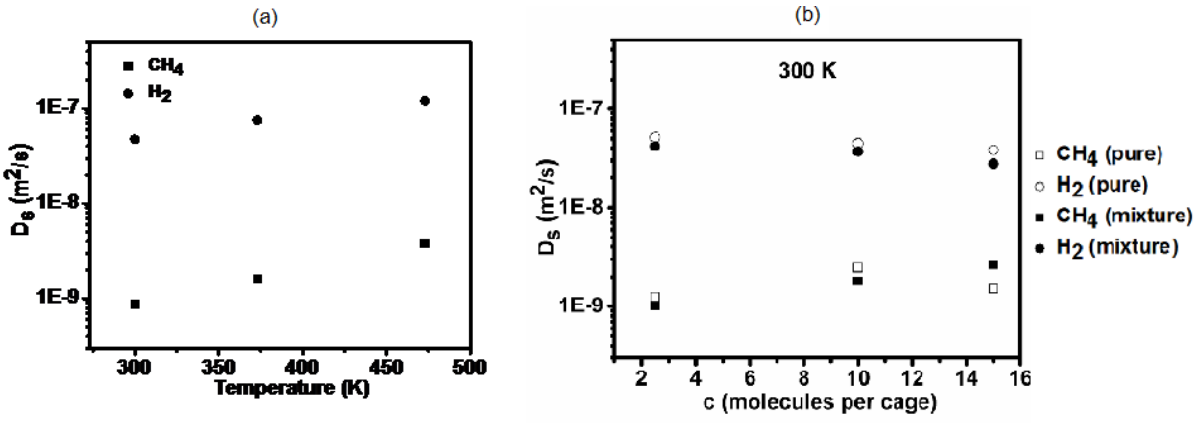

Fig. 7 a) The D_s of CH_4 and H_2 in H_2/CH_4 mixture at different temperatures at a very low loading (0.25 CH_4 + 0.25 H_2 molecules/cage) in ZIF-90. b) D_s as a function of the loading for the pure components CH_4 and H_2 as well as the equimolar adsorbed H_2/CH_4 mixture at 300 K.

Higher concentration of guest molecules to be seen in Fig. 7b shows that the D_s values do not change very much with changing loading, even if the loading is increased from 2 molecules per cage up to 15 molecules per cage. This supports the idea of an extrapolation to lower concentration of H_2. At higher loadings, the D_s of CH_4 increases slightly with increasing loading, while that of H_2 is slightly decreasing. Remarkably, the self-diffusion coefficients D_s for the pure single component adsorbate and for the adsorbed mixture are not very different from each other if the total amount of adsorbed molecules is the same even for loadings up to 15 molecules per cage. *e.g.,* the D_s of H_2 is only slightly smaller if half of the H_2 molecules are replaced by the

heavier CH_4 molecules. At high loading, the D_s of CH_4 is somewhat larger in the mixture when half of the CH_4 molecules have been replaced by the lighter H_2. If this is true even at higher loadings, then this finding strongly supports the assumption that the D_s in the low pressure region (1 bar like in [17]) does not depend on the concentration ratio of the mixture. Thus, our results of adsorption and diffusion data - which we need for the calculation of permeation selectivities - can be extended to non-equimolar feed mixtures.

2.2.2 Probability densities

The probability densities of particle locations for the adsorbed H_2/CH_4 mixture are plotted in Fig.8. The red dots refer to the sites of H_2 and the green dots represent the sites of CH_4 (colors in the web) in snapshots taken every 100 steps from the last 200000 steps in MD simulations to describe the position probability of methane and hydrogen during simulation time.

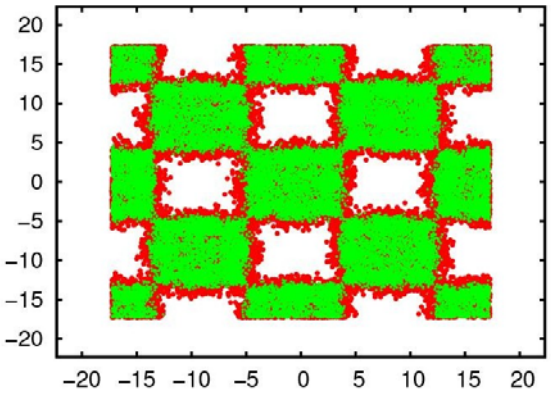

Fig. 8 The density distributions of the two kinds of guest molecules at 300 K for 5 CH_4 + 5 H_2 molecules per cage. Red: Hydrogen, green: methane.

It can be seen that at this quite high density, the H_2 molecules have higher probability to reside close to the cavity walls while the CH_4 molecules are distributed over the whole cavity. For low adsorbate densities, the statistics is too poor for such a density plot. Therefore, the structure of the adsorbed mixture at low density has been investigated by the radial distribution function (RDF). The results can be seen in Fig. 9.

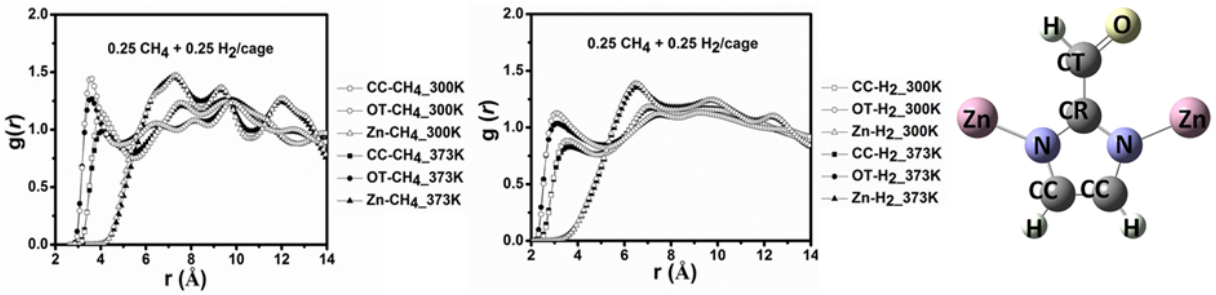

Fig. 9 RDFs of the CH_4 and H_2 with selected atoms in ZIF-90 at 300 K and 373 K at the low guest molecule concentration of 0.25 CH_4 + 0.25 H_2/cage and organic linker.

At low adsorbate density, favorite adsorption sites of both CH_4 and H_2 are the oxygen atoms of the aldehyde group of the linker in the ZIF-90 lattice. Other sites of high probability are CC that means the organic linker in agreement with many other ZIFs and with the single gas CH_4 in ZIF-90 in the previous work [9,10,13,18,19,21,22].

2.2.3 Permeability

To compare the results with the experiment, the permeability is calculated from the adsorption and diffusion data by the following equation. The results are shown in Fig. 10. It is shown that the simulation results of this work for the permeance show a rather good agreement with the experiment of [17]. While the permeance of H_2 agrees quite well with the experiment, the permeance of CH_4 is slightly overestimated. Atci's work [11] which uses a rigid framework model for the calculation, yields lower values of the permeance by about half an order of magnitude due to the underestimated D_s.

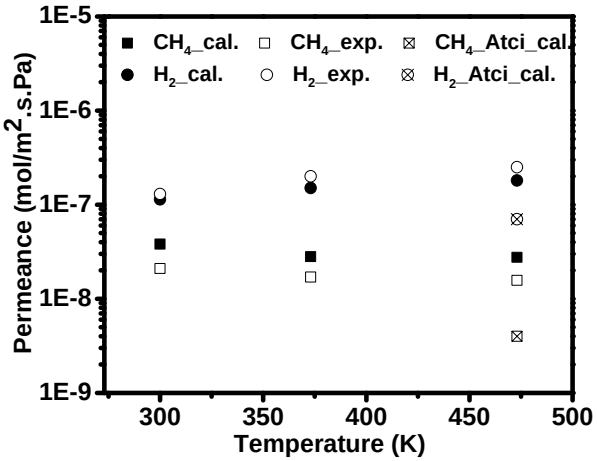

Fig.10 Comparison the calculated membrane permeances for the equimolar H_2/CH_4 mixture in comparison with the permeation experiment [17] and Atcis work [11].

In addition, from adsorption and diffusion selectivities, the separation factors are also evaluated through the following equation and then they can be compared with the separation factor from the permeation experiment on a ZIF-90 membrane at the three temperatures.

Table 3 Comparison of the membrane selectivity of the H_2/CH_4 mixture of our calculation and the membrane permeation experiment of Huang et al. [17].

	Separation factor H_2/CH_4	
Temperature	Experiment	Calculation
300 K	7	3.9
373 K	11	6.5
473 K	15.2	9.1

Table 3 shows a comparison of the membrane selectivity of the H_2/CH_4 mixture of our calculation and the membrane permeation experiment of Huang et al. [17]. The results are in fair agreement although the calculated values are smaller. This can be explained by the assumption of a perfect crystal framework as mentioned in previous work which leads to a lower separation factor than the experimental one of Huang et al. [17].

2.2.4 Gate opening effect

To explore the influence of the amount of guest loading on the framework, CH_4/H_2 (ratio 1:1) mixtures were assumed to be adsorbed into ZIF-90 at different concentrations: 0.5, 2.5, 10, 15, 30 total molecules/cage. The resulting window size as a function of loading is shown for two temperatures in Fig. 11.

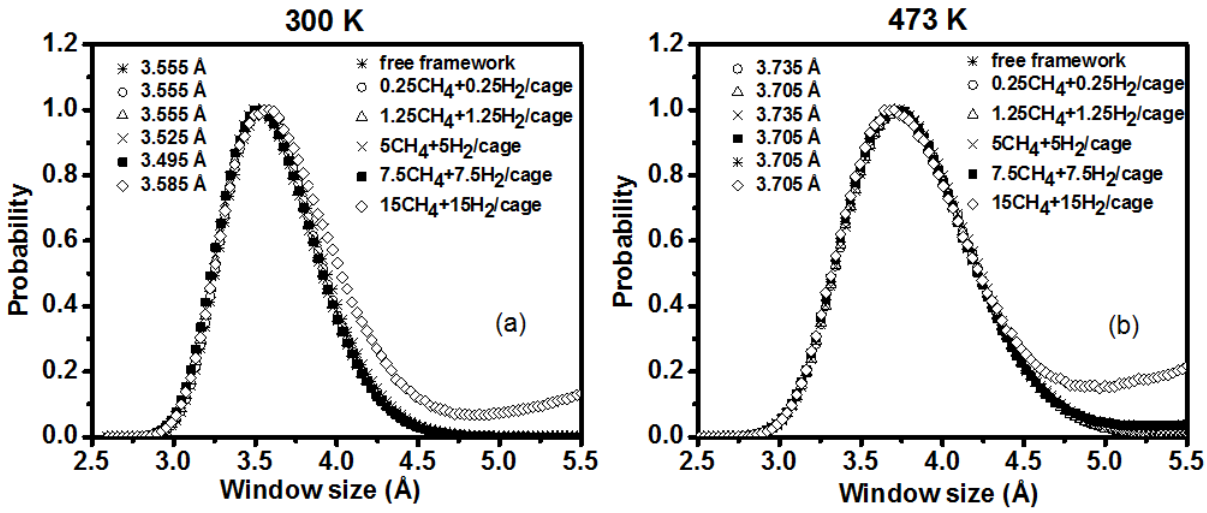

Fig. 11 The probability distribution of the window size in two different temperatures a) 300K and b) 473 K.

Fig. 11 shows that the increase of loading of guest molecules did not affect significantly the structure of the framework. Specifically, the window sizes of ZIF-90 at 300 K with and without guest molecules inside are nearly unchanged, around 3.5 Å and agree with its value in the XRD structure. In contrast with this it becomes around 3.7 Å by a temperature change to 473 K which is 0.2 Å larger than the XRD experiment reported at 300 K. Again, the results fit well together with the previous study that there is no gate-opening effect for loadings of CH_4 inside ZIF-90 at 300K even up to 15 CH_4 per cage [15].

3. Gate Opening, Diffusion and Adsorption of CO_2 and N_2 Mixtures in ZIF-8

(Accepted by Journal of Physical Chemistry C, 120 (41), (2016), 23458-23468.)

In the present work the adsorption and diffusion of CO_2/N_2 mixtures in ZIF-8 are examined by both MD with flexible lattice and GEMC with rigid lattice. Also dynamical properties of the adsorbed molecules in mixtures and their influence on the flexible lattice are investigated. Particularly, the question if the classical MD simulations will give a gate opening effect also for this system is examined. GEMC, different from GCMC, yields directly the equilibrium between gas phase, in which the pressure can be calculated from an equation of state, and the adsorbed phase of the mixture while in GCMC only the adsorbed phase is included in the simulation. The influence of the temperature on the adsorptive CO_2/N_2 separation is investigated. The self-diffusion coefficients of CO_2 and N_2 are evaluated, so that the diffusion selectivity can be calculated. From the adsorption and diffusion selectivity the membrane selectivity can be obtained.

3.1 Gibbs Ensemble Monte Carlo (GEMC) simulations

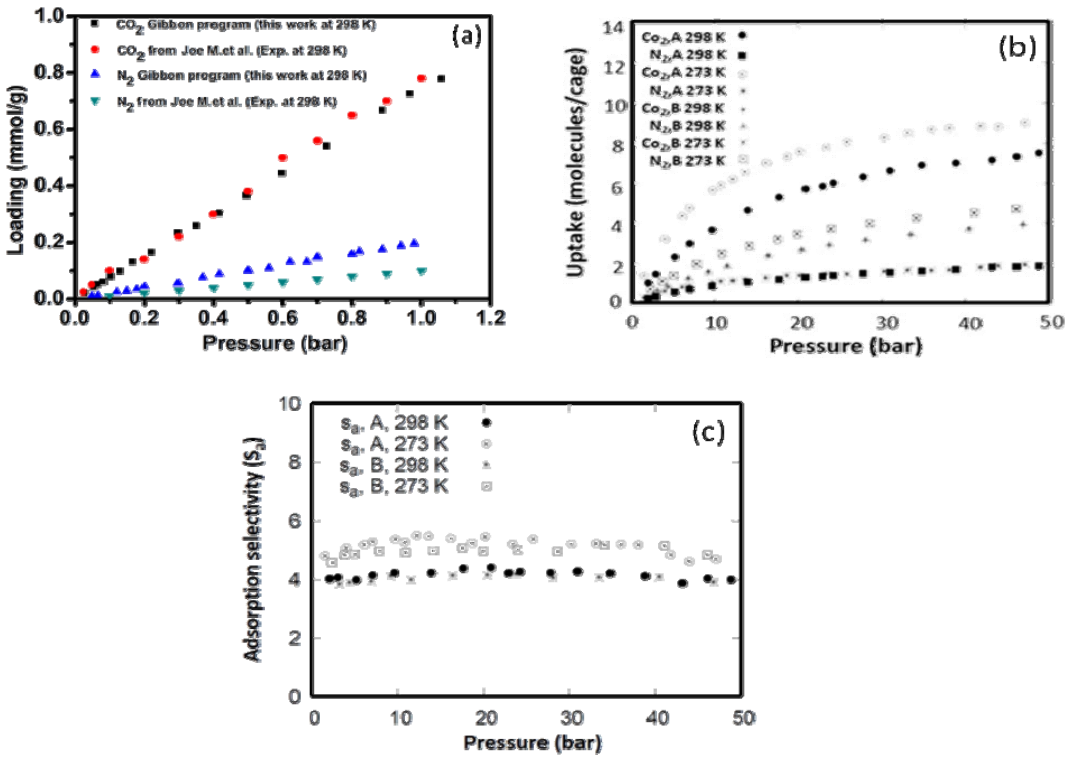

Fig. 12 a) Adsorption isotherms for single gas CO_2 and N_2. b) Adsorption isotherms for the equimolar (in the gas phase) mixture CO_2/N_2. c) Adsorption selectivity CO_2/N_2 as a function of the gas-phase pressure for the equimolar (in the gas phase) mixture CO_2/N_2.

The adsorption selectivity CO_2/N_2 at 298 K and 1 bar as calculated by Ideal Adsorbed Solution Theory (IAST) from pure species adsorption isotherms is given. The adsorption selectivity is low and does not depend upon the CO_2/N_2 ratio. However, the exact value of the adsorption selectivity is difficult to derive from Fig. 12c of ref. [22] because of its relatively small value for ZIF-8. The estimated adsorption selectivity in ref. [22] is the order of our value, but it seems to be somewhat larger. This is clearly due to the stronger adsorption of N_2 in our model. In ref. [22] the adsorption selectivity CO_2/N_2 at 298 K is calculated from pure component adsorption data by IAST as a function of the pressure. A slight decrease of the selectivity with increasing pressure has been found. The average value of the selectivity agrees well with our value. Neither in ref. [23] nor in ref. [22] mixture simulations have been carried out. The CO_2/N_2 adsorption selectivity depends much more on the temperature than on the pressure. For both temperatures it seems to be slightly higher for densities around $4x10^{-4}$ molecules per Å than for the other densities, but this difference is still too close to the magnitude of the fluctuations to be sure.

3.2 Molecular Dynamics (MD) simulations

The self-diffusion coefficients are shown in Fig 13. All self-diffusion coefficients D_s of CO_2 and N_2 as single-component gas as well as in the mixture CO_2/N_2 were found to be around 10^{-9} to 10^{-12} m^2/s and follow a similar trend.

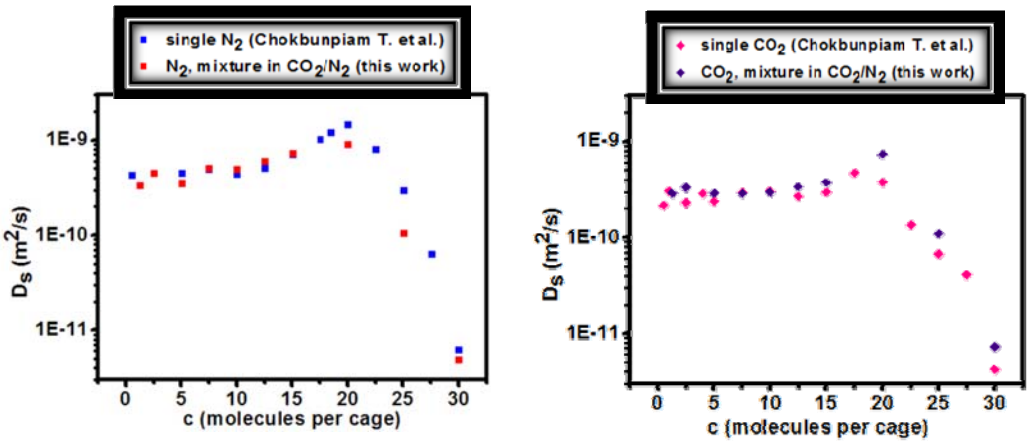

Fig. 13 Molecular self-diffusion of CO_2 and N_2 at 300 K for the single-component loadings 0.5-30 molecules/cage and the mixed gas loadings $0.5CO_2$:$0.5N_2$ to $15CO_2$:$15N_2$ molecules/cage in ZIF-8 framework by MD simulations.

For the single-component gases, D_s did not change significantly at low loadings but for loadings above 18.44 and 20.0 molecules/cage, respectively, [18,19] the D_s values of N_2 and CO_2 drop dramatically down to 10^{-12} m^2/s. However, in the case of mixtures, already at a mixed loading of $7.5CO_2$:7.5 N_2, the D_s exhibited a strong decrease from 10^{-9} to 10^{-12} m^2/s. That means, the decrease of D_s happens for the single-component gases at loadings below 18.44 and 20.0 molecules/cage while in the mixture it occurs at approximately 15 molecules (7.5 CO_2:7.5 N_2) molecules/cage or when the total number of guest molecules is 15 molecules/cage. These results are interesting in connection with the transition structure and the change of the window size as function of loading as shown in the above section. Obviously, with increasing loading of ZIF-8, the mutual blocking by molecular collisions has a stronger influence than the gate opening.

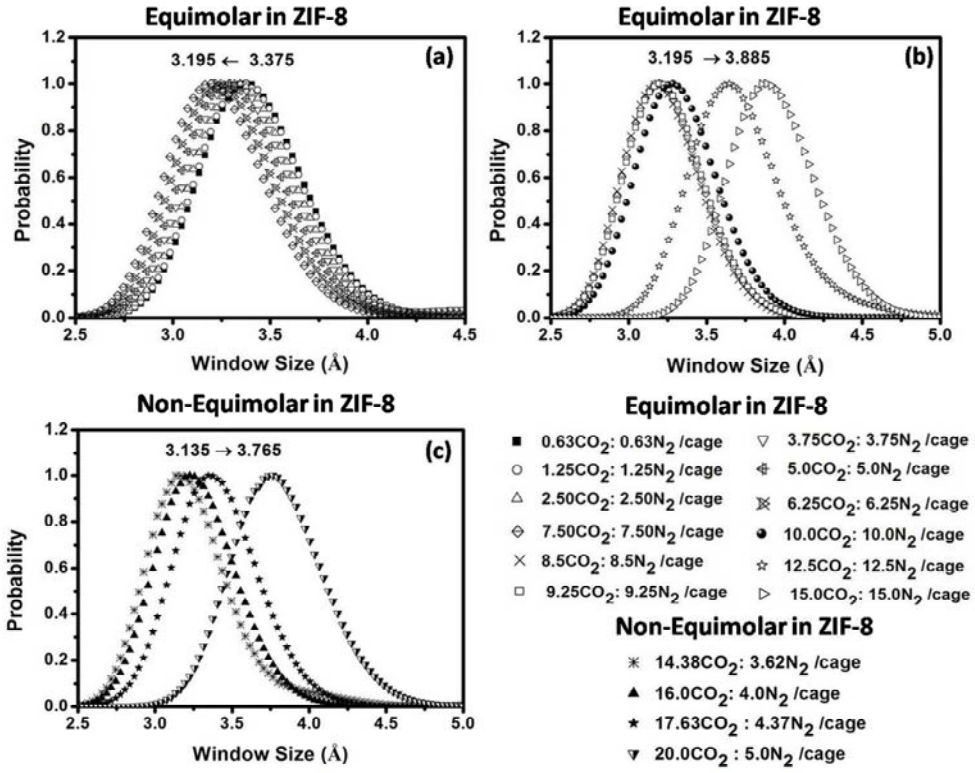

Fig. 14 The distribution of window size (6-membered rings) of ZIF-8 for mixture loadings of $0.5CO_2/0.5N_2$ to $15CO_2/15N_2$ molecules/cage at 300 K. a) Slight decrease of the window size with increasing loading. b and c) Large increase of the window size with increasing loading.

In Fig. 14 shows the change of the window size with the loading for mixtures of CO_2 and N_2. At low loadings (a) the window sizes become slightly smaller from 3.375 to 3.195 Å. However, from 10 CO_2/10 N_2 to 15CO_2/15N_2 for equimolar adsorbed mixtures in ZIF-8 (b) a gate opening up to more than 3.7 Å can be observed. For the adsorbed mixture of the composition CO_2:N_2 = 4:1 in ZIF-8 (c) the gate opening starts at 16 CO_2/4 N_2. Therefore, the window sizes from single-component gases CO_2, N_2 and CO_2/N_2 mixture adsorption can be ordered [18,19] CO_2 > CO_2/N_2 > N_2 (4.125 > 3.885 > 3.585). These results confirm that CO_2 has a much larger effect on the window size of the ZIF-8 framework than N_2. Adsorbed N_2 and CO_2 as single-component gases at 298 K were shown by Chokbunpiam et al. in ref. [19,20] to lead to the gate opening at loadings of 18.44 and 22.5 molecules/cage, respectively. For the equimolar adsorbed mixture CO_2/N_2 in ZIF-8 gate opening was found at 10 CO_2 / 10 N_2 *i.e.* for 20 guest molecules/cage. Thus gate opening is found for a mixed loading which is closer to the transition loading of pure N_2 than to that of pure CO_2.

3.3 Membrane selectivity by GEMC and MD simulations

The membrane selectivity was proposed in refs [4, 24-26]. $\alpha_{ij}^{membrane} = \alpha_{ij}^{diffusion} \times \alpha_{ij}^{adsorption}$, with the diffusion selectivity $\alpha_{ij}^{diffusion}$ as the ratio of the self-diffusitivities of the species i and j, and the adsorption selectivity $\alpha_{ij}^{adsorption}$ as the ratio of the adsorbed amounts of i and j. Therefore, we have alternatively tried to simulate a mixture that is equimolar in the ZIF-8 box like in the MD simulations. This is difficult because many trials are necessary to achieve this composition. To adjust an equimolar mixture in the gas phase for the final equilibrium state at each density is much easier. We investigated at 298 K the mixture, equimolar in ZIF-8 at concentrations of 1.29 and 1.60 guest molecules per cage. For 1.29 guest molecules per cage the density in the gas phase was 7.80 x 10^{-5} A^{-3} and the ratio of the molecule numbers of the two sorts was 0.265 in the gas phase. The adsorption selectivity was found $\alpha_{ij}^{adsorption}$ = 3.96, with *i* meaning CO_2 and *j* meaning N_2. With the diffusion selectivity, $\alpha_{ij}^{diffusion}$ = 0.865, thus the membrane selectivity, $\alpha_{ij}^{membrane} = \alpha_{ij}^{diffusion} \alpha_{ij}^{adsorption}$ = 0.865 x 3.96 = 3.43, This value is somewhat lower than the value 5.72 found in [27] in the low-pressure limit. For 1.60 guest molecules per cage the density in the gas phase was 10.1 x 10^{-5} A^{-3} corresponding to a pressure of 4.12 bar. The adsorption selectivity was $\alpha_{ij}^{adsorption}$ = 3.91 with *i* meaning CO_2 and *j* meaning N_2. With an approximately interpolated diffusion selectivity of $\alpha_{ij}^{diffusion}$ = 0.8, thus the membrane selectivity to be roughly $\alpha_{ij}^{membrane}$ = 3.1. This is in acceptable agreement with results of Diestel et al. [28] who found in mixed gas permeation on a supported ZIF-8 membrane a separation factor CO_2/N_2 ≈ 2 from mixed gas permeation studies.

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Output of the research

Publications

1. P. T. Vo, T. Chokbunpiam, S. Fritzsche, T. Remsungnen, C. Chmelik, J. Caro, S. Hannongbua. “Methane in Zeolitic Imidazolate Framework ZIF-90: Adsorption and Diffusion by Molecular Dynamics and Gibbs Ensemble Monte Carlo”, Microporous and Mesoporous Material, 235 (2016), 69-77.

2. T. Chokbunpiam, S. Fritzsche, C. Chmelik, , J. Caro, W. Janke and S. Hannongbua “Gate opening, Diffusion and Adsorption of CO_2 and N_2 mixtures in ZIF-8”, Journal of Physical Chemistry C, 120 (41), (2016), 23458-23468.

3. T. Chokbunpiam, S. Fritzsche, C. Chmelik, , J. Caro, W. Janke and S. Hannongbua “Importance of ZIF-90 Lattice Flexibility on Diffusion, Permeation and Lattice Structure for an adsorbed H_2/CH_4 Gas Mixture – A Re-Examination by Gibbs Ensemble Monte Carlo and Molecular Dynamics Simulations”, Journal of Physical Chemistry C, 121 (19) 2017, 10455-10462.

APPENDIX

THE JOURNAL OF PHYSICAL CHEMISTRY C

Article

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Gate Opening, Diffusion, and Adsorption of CO_2 and N_2 Mixtures in ZIF-8

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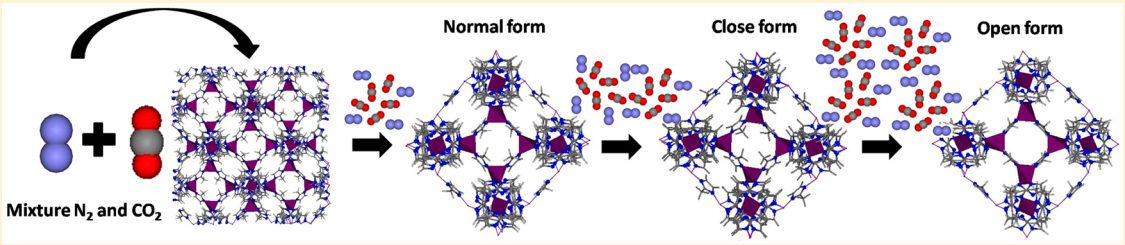
Supporting Information



ABSTRACT: Diffusion and adsorption of CO_2/N_2 mixtures in the zeolitic imidazolate framework ZIF-8 are investigated by molecular dynamics (MD) and Gibbs ensemble Monte Carlo (GEMC) simulations. Structural changes called "gate opening" could be found for the adsorbed single-component gases and for the mixture. The gate opening appears for the mixture at a total number of guest molecules per cavity between that for the pure CO_2 and that for the pure N_2 but closer to that of N_2 which is lower. Due to the stronger dependence of CO_2 adsorption upon the temperature in comparison with N_2, the adsorption selectivity is predicted to be higher at lower temperatures, which is in accordance with experimental findings.

1. INTRODUCTION

Porous materials play an increasing role in research and industry. Particularly, during the past decade metal−organic frameworks (MOFs, see refs 1 and 2) came into the focus of interest because of their great diversity, the big pores, and the possibility of custom-made design. Some of them have the highest internal surface areas per gram of all porous materials known to date (see Li et al.[2]). They consist of metal ions or metal oxide clusters that are connected by organic linkers forming porous frameworks. Replacing the organic linkers, new structures can be created and also exchange of the metal ions or metal ion clusters can change the properties of MOFs thus giving the possibility of tailoring the MOFs to specific applications. For example, Kwon et al.[3] and Krokidas et al.,[4] respectively, could show that replacement of Zn^{2+} with Co^{2+} in ZIF-8 (resulting in ZIF-67 framework) enhanced significantly the propylene/propane separation.

But, for technical applications, also a high stability against thermal and chemical conditions of use and against pressure changes is required. With respect to the stability a subgroup of the MOFs, the zeolitic imidazolate frameworks (ZIFs), are very promising. Many of them have high thermal and chemical stability (see Park et al.[5]) that makes them interesting materials for potential industrial purposes.

Besides experiments, simulations are important tools for the exploration of such materials. Simulations are safe, comparatively cheap and well-suited to understand or forecast properties of guest molecules in MOFs. They are able to vary conditions to identify reasons for effects. Examples are simulations with rigid and flexible MOF lattice for comparison.

An interesting feature of many MOFs, that is also important for applications, is the lattice flexibility that is much larger than that of other porous materials, e.g., zeolites.[6−11] As an example, in refs 6 and 7 it could be shown that this can result in opening of bottlenecks in the lattice of the MOF Zn(tbip) at high guest molecule concentrations resulting in interesting patterns of the dependence of the self-diffusion coefficient upon the guest molecule concentration. But, even under ambient conditions, the fluctuating size of the so-called windows, that connect adjacent cavities, can have drastic consequences. In Hertäg et al.[9] it turned out that the diffusion selectivity for a CH_4/H_2 mixture in ZIF-8 was changed by several orders of magnitude due to this effect. The lattice of ZIF-8 is quite flexible so that molecules slightly larger than the average window (bottleneck)

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diameter (3.4 Å from Rietveld refinement) can diffuse due to the window "breathing".[9,10] This concept could be reproduced only in flexible lattice simulations with appropriate parameters like, e.g., those from the Amber force field[12] or by Haldoupis et al. in ab initio molecular dynamics (MD),[10] while parameters from the also well-established Dreiding force field[13] yield a too stiff lattice (see Hertäg et al.[9]). Hence, the choice of appropriate interaction parameters is very important, and not easy. Additionally, the correct simulation of the lattice vibrations requires the definition of about 10 000 elastic bonds, angles, and dihedral angles for an MD simulation box. The consequence is a big programming effort and requirement of computer time. Therefore, simulations in the rigid lattice may appear to be attractive, but this can lead to a diffusion behavior which is far from the experimental findings as shown, e.g., by Hertäg et al.[9]

Moreover, the lattice flexibility can lead to such surprising effects as found by the group of Kapteijn for ethane/ethylene adsorption in ZIF-7 (see refs 14 and 15). It consists in a change of the lattice shape of ZIF-7 that opens bottlenecks and enables larger molecules such as ethane to enter the ZIF-7 structure more easily. The effect was named "gate opening". By density functional theory (DFT) calculations it could be shown by van den Bergh et al.[15] for this system and by Zheng et al.[16] for ethane in ZIF-8 that this gate opening is, in some cases, based on quantum effects. Hence, it could not be reproduced in classical MD simulations, even not with flexible lattice, for ethane in ZIF-8 (see Chokbunpiam et al.[17])

ZIF-8 is a well-known member of the ZIFs. In ZIF-8, Zn^{2+} ions are interconnected by methylimidazolium anions (mim^-) forming an SOD lattice of the composition $Zn^{2+}(mim^-)_2$. Many experimental and computational studies of ZIF-8 have been published already, e.g., refs 9, 11, 16−35.

Moggach et al. described in ref 26 a structure of ZIF-8 that has been observed at 1.47 GPa under loadings of up to 41 methanol molecules per unit cell. This high-pressure structure shows larger pore volume and larger diameter of the windows that connect adjacent cavities and corresponds to a gate-opening effect. The change is reversible. In order to understand this phenomenon Fairen-Jimenez et al. investigated in ref 27 the high-pressure structure, called ZIF-8HP, by experiment and grand canonical Monte Carlo (GCMC) simulation, and the results are compared with those from the ZIF-8 structure at ambient pressures which is named ZIF-8AP. The authors compared the measured adsorption isotherm of N_2 in ZIF-8 by use of separate GCMC simulations with rigid lattice for the two structures ZIF-8AP and ZIF-8HP and show that at low pressure the simulated isotherm for the ZIF-8AP structure and at high pressure the simulated isotherm for the ZIF-8HP structure agree well with the experiment. It is concluded, therefore, that in reality increasing concentration of N_2 causes a phase transition from ZIF-8AP to ZIF-8HP. The transition itself cannot be simulated with rigid lattice GCMC.

In Zhang et al.,[28] this gate-opening effect was first found in classical MD simulations for N_2 in ZIF-8 at low temperature. This gate opening could also be found by Chokbunpiam et al.[19] at ambient temperature and at a loading that agreed with the experiment. The gate opening was caused by a reorientation of the linker molecules. Other theoretical studies about gate opening that is caused by linker rotation and which can be also called "swinging door motion" or "saloon door motion" include refs 4, 10, and 36. This saloon door motion could also be examined experimentally by Kolokolov et al.[37] for benzene and by Casco et al.[38] upon N_2.

Since carbon dioxide is a very important gas in many chemical processes and on the other hand a prominent greenhouse gas, the behavior of CO_2 in ZIF-8 is very interesting with respect to a possible use of ZIF-8 for storage or for separation of CO_2. Particularly, adsorption at higher pressure is of interest for pressure-swing separations because exposure of the loaded ZIF to ambient pressure is sufficient to release the largest part of the guest molecules and to make the ZIF ready for repeated use. Fairen-Jimenez et al.[29] investigated the adsorption of some gases including CO_2 by experiment and rigid lattice GCMC simulations. For CO_2 at 273 K both structures ZIF-8AP and ZIF-8HP give similar adsorption isotherms for the whole range of pressure (see Figure 4 of this paper,[29] lowest curve on the right). These similar isotherms do not allow drawing conclusions about the existence of gate opening for CO_2. Therefore, in Chokbunpiam et al.[20] this question has been examined by MD simulations with flexible lattice. It has been shown that a gate opening happens for CO_2 in flexible ZIF-8 at 300 K only for loadings of more than 22 CO_2 molecules per cavity which corresponds to a high pressure which would be above the gas−liquid transition pressure in a connected gas volume. In Venna and Carreon[30] the use of ZIF-8 in a membrane for the separation CO_2/CH_4 is investigated experimentally. In Zhang et al.[31] it is described how the adsorption of CO_2 in ZIF-8 can be enhanced by a special treatment of the ZIF sample. Experimental adsorption isotherms of CO_2 in ZIF-8 are also shown in refs 21−25, 29, 31−34. All of these papers did also GCMC simulations, and each group found parameters that give agreement with the values of their measurements, respectively. A comparison of some of these quite different isotherms is given by Chokbunpiam et al.[20] In refs 18, 22, and 33 also the diffusion of CO_2 in ZIF-8 is investigated experimentally and by simulations. Experimental values from Chmelik[35] have also been compared with simulation results of Chokbunpiam et al.[20] In ref 11 Zhang et al. examine the adsorption and diffusion of CO_2 in ZIF-8 at high pressure (up to 100 bar) by simulations. The importance of the lattice flexibility for diffusion is demonstrated. Gate opening is not mentioned in ref 11. The diffusion of CO_2 in ZIF-8 is also examined by ab initio molecular dynamics (AIMD) calculations by Haldoupis et al.[10]

Nitrogen as the major constituent of air is of high interest for the investigation of mixtures with CO_2. Several papers report the adsorption of nitrogen in ZIF-8. By Pérez-Pellitero et al.[23] the adsorption properties of CO_2, CH_4, and N_2 in ZIF-8 at 303 K have been examined. The adsorption of N_2 and of CO_2 in ZIF-8 and modified ZIF-8 are also investigated by Zhang et al.[31] where the single-component adsorption isotherms are found from simulations, while that of the mixture were calculated from single-component data by ideal absorbed solution theory (IAST), but not from simulations as is done in the present paper. Experimental isotherms for the adsorption of CO_2 and N_2 (single component) for low pressures up to 1 bar are reported by McEwen et al.[21] Like in ref 31 mixture data are predicted in ref 21 by IAST, but not from simulations. The simulations of the adsorption isotherms of Chokbunpiam et al.[20] show excellent agreement for CO_2 with those of McEwen et al.[21]

Battisti et al.[34] investigated the adsorption of several mixtures including CO_2/N_2 in different ZIFs including ZIF-8 by GCMC and MD at 298 K. For the GCMC simulations the lattice was

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Table 1. Values of the Adsorption Constant K at 298 K from Gibbon Compared with Values Computed from Published Data of Other Papers[a]

	this work	McEwen et al.[b]	Simmons et al.[c]	Zhang et al.[d]	Pérez-Pellitero et al.[e]	Liu et al.[f]	Pusch et al.[g]
N_2, pure	0.26	0.14	0.30	0.15	0.11		
N_2 in mix	0.25	0.14		0.14			
CO_2, pure	1.06	1.05		0.61		0.62	0.94
CO_2 in mix	0.99	1.05		0.61			

[a]The values for K are given in molecules per cage and per bar. [b]Ref 21. [c]Ref 24. [d]Ref 31. [e]Ref 23. [f]Ref 32. [g]Ref 33.

assumed to be rigid as in most adsorption simulation studies. The MD simulation was carried out with flexible lattice applying the Dreiding force field. The lattice structure has not been investigated, e.g., with respect to the gate-opening effect. Because the independent variable of state in GCMC is the chemical potential rather than the pressure, an additional relation between the chemical potential and the gas-phase pressure is needed. Battisti et al.[34] used the van der Waals equation of state for this purpose. The van der Waals equation is known to be less accurate than, e.g., the Peng−Robinson equation. This may lead to some inaccuracy in the adsorption results. For the membrane selectivity or permeation selectivity of CO_2/N_2 in the low-pressure limit a value of 5.72 is reported by Battisti et al.[34] Structural details like radial distribution functions or adsorption sites have not been investigated in ref 34.

In the present paper the adsorption and diffusion of CO_2/N_2 mixtures in ZIF-8 are examined by both MD with flexible lattice and Gibbs ensemble Monte Carlo (GEMC) with rigid lattice. In MD, dynamical properties of the adsorbed molecules in mixtures and their influence on the flexible lattice are investigated, which was not done in refs 31 and 34. Particularly, the question whether the classical MD simulations will give a gate-opening effect also for this system is examined.

The influence of the temperature on the adsorptive CO_2/N_2 separation is investigated. This adsorptive CO_2/N_2 separation is of special interest in the so-called "post combustion" strategy to extract CO_2 from power plant exhaust gases after steam has been removed by condensation.

The self-diffusion coefficients of CO_2 and N_2 are evaluated so that the diffusion selectivity can be calculated. From the adsorption and diffusion selectivities the membrane selectivity can be obtained.

2. COMPUTATIONAL DETAILS

2.1. Interaction Parameters. For the lattice atoms of the MOF and for CO_2, the interaction parameters are the same as in Chokbunpiam et al.[20] They showed good agreement of the simulated self-diffusion coefficient of CO_2 in ZIF-8 with experiments, and also the adsorption isotherms were found to be within the range of various experimental isotherms. Best agreement was found with the isotherm of McEwen et al.[21] For N_2 in ZIF-8, the same parameters as in Chokbunpiam et al.[19] are used. In ref 19 the structural phase transition in ZIF-8 has been investigated, but not the adsorption of guest molecules.

To check the interaction parameters, tests at low pressure are carried out. In order to include also the results of McEwen et al.[21] (where the adsorption has been investigated only at low pressure) in our comparison, we used the linear low-pressure part of the adsorption isotherm to check the consistency of our parameters by experimental adsorption results.

As the uptake u of N_2 and CO_2 in ZIF-8 at 298 K follows at low pressures p a linear law (analogous to Henry's law)

$$u = Kp \tag{1}$$

it might be interesting to compare for pressures up to 5 bar the adsorption constant K from different papers with K values obtained in the present paper by simulation. Note that the concept of the Henry law comes from dissolution of gases in liquids, and in such applications, the Henry constant is usually defined in a way that is slightly different from our K.

The validation of the used parameters by comparing values of K of this paper with those obtained from published adsorption isotherms is presented in Table 1 and discussed in the Results and Discussion, section 3.6.

2.2. Molecular Dynamics Simulations. The zeolitic imidazolate framework-8 (ZIF-8) structure, has been derived from X-ray diffraction (XRD) data by Park et al.[5] The Mercury program has been used to construct a lattice containing eight unit cells as shown in Figure 1.

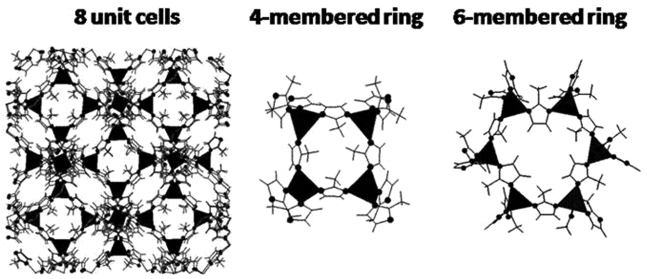

Figure 1. ZIF-8 structure consisting of zinc (Zn^{2+}, tetrahedra) which is connected by imidazolate linkers that consist of nitrogen (N, circle), carbon (C, line), and hydrogen (H, line).

These eight unit cells of the ZIF-8 form the cubic simulation box (edge length 33.982 Å) for the MD simulations by the DL_POLY software. We used flexible models for ZIF-8 like in earlier papers of Chokbunpiam et al.[17,20] The parameter data for N_2 and CO_2 were taken from Potoff et al.[39] and Liu et al.[32] First, simulation in the isochoric−isothermal ensemble (NVT) is carried out to equilibrate the system for 5 ns. Then, the evaluation part of the run of 25 ns is done in the microcanonical ensemble (NVE) with an average temperature of 298 K which is close enough to 300 K. The integration time step is 2 fs, the VDW interaction cutoff was 14 Å, and Ewald summation was done. The stability of the lattice for our parameters without fixed box size was tested by NPT simulations of the empty lattice at 1 bar as already reported by Chokbunpiam et al.[17]

The window size fluctuations and the diffusion coefficients of N_2 and CO_2 as mixture in ZIF-8 are investigated. Finally, we compare our simulation results with the experimental data and computer modeling.

2.3. GEMC. Gibbs ensemble Monte Carlo simulations (GEMC, see Panagiotopoulos[40]) of the adsorption isotherm

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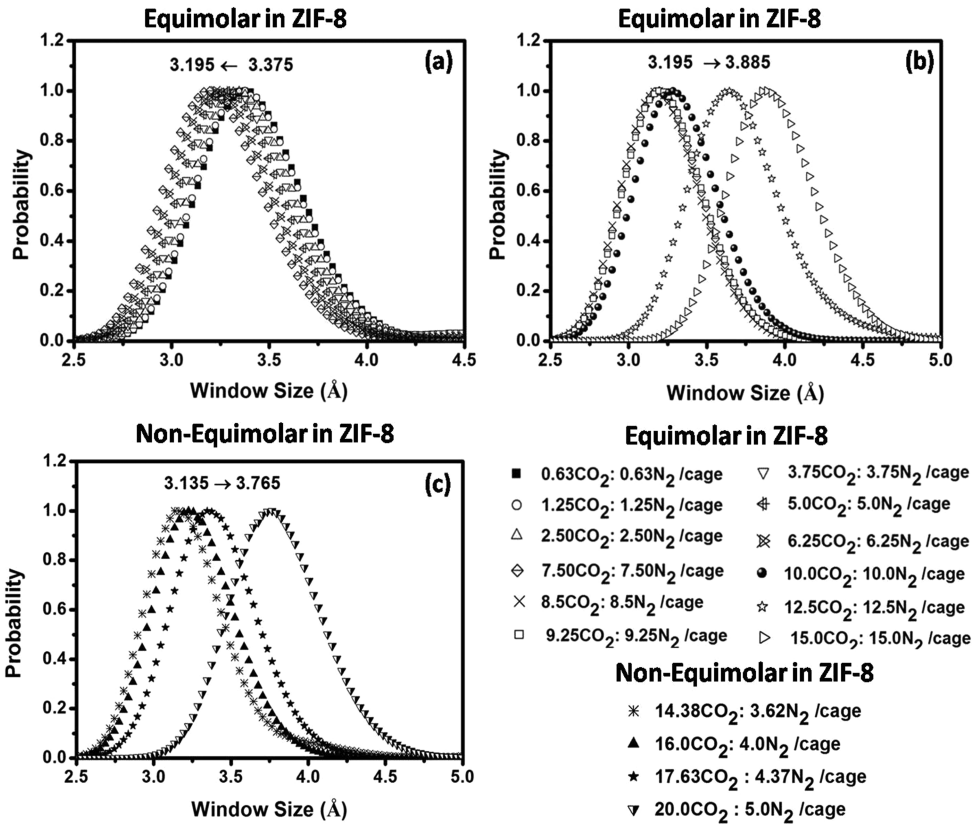

Figure 2. Distribution of the window size (six-membered rings) of ZIF-8 for mixtures with different loadings at 300 K. Slight decrease of the window size with increasing loading (a). Large increase of the window size with increasing loading (b and c).

are done using the homemade Gibbon software that has been used successfully by Chokbunpiam et al.[20] for pure CO_2 already. In GEMC, the equilibrium between the gas and adsorbed phases is established by particle exchange between two simulation boxes, box A containing a free bulk gas and box B containing the porous crystal with the adsorbed phases.

GEMC directly yields the equilibrium between the adsorbed phase of the mixture and the gas phase, in which the pressure can be calculated from the density by an equation of state. In GCMC, only the adsorbed phase is included in the simulation and the calculation of the pressure must be done by the virial theorem that is not very accurate for nonspherical, charged particles at high pressure, or alternatively, an additional relation between chemical potential and pressure would be needed.

The adsorption isotherm is normally given in form of uptake as a function of the pressure. GEMC simulations yield the uptake as a function of the density in the connected gas phase. Agreement with the common form of description requires the calculation of the pressure in the gas phase. For low pressures up to about 1 bar, the ideal gas law can be used. To calculate the pressure at higher gas-phase densities, we have used the Peng−Robinson equation of state[42] for both pure substances and also for the mixture. The fact that the density in the gas phase is obtained without any detour that would use, e.g., the chemical potential, which cannot be measured directly, is the main advantage of the GEMC method over GCMC.

A phase transition of gas/liquid happens for pure CO_2 at 298 K at about 64 bar in the free bulk gas. Our Gibbon software is not able to simulate states that include gas/liquid coexistence in the gas-phase box because of the periodical boundary conditions. To be sure to avoid any artifacts like existence of droplets, etc., we did GEMC for pure CO_2 and for the mixture that contains CO_2 only in the pressure range up to 50 bar.

The GEMC simulations are carried out with rigid lattice and rigid molecules because in several papers it has been found already that the adsorption isotherm is much less sensitive against the approximation of a rigid lattice than diffusion[11,41] as long as no structural transitions (e.g., gate opening) happen. Hence, before GEMC with rigid lattice can be done, a structural phase transition for the system and the pressure range that is examined must be excluded. This can be done, e.g., by MD simulations with flexible lattice. In the present paper, GEMC is done only at pressures far below the pressure where gate opening is observed.

One advantage of rigid lattice Monte Carlo (GEMC or GCMC) in comparison to MD with flexible lattice is that the position changes of the molecules per simulation step in the GEMC are about 2 orders of magnitude larger than in MD with flexible lattice, which leads to much better statistics. Moreover, in flexible lattice MD, all the forces connected with elastic bonds, elastic angles, and elastic torsion in the lattice must be calculated in each step. They are very computer time expensive because they include three-body forces and four-body forces. Thus, Monte Carlo with flexible lattice would not be effective and, hence, cannot be found in the literature for adsorption simulations. On the other hand, MD is necessary to investigate time-dependent phenomena, e.g., diffusion, lattice vibration, etc.

We used the same interaction parameters for both the GEMC simulations and the MD simulations in this paper.

In each run the random starting situation is relaxed to equilibrium by an equilibration period of typically 10 million to

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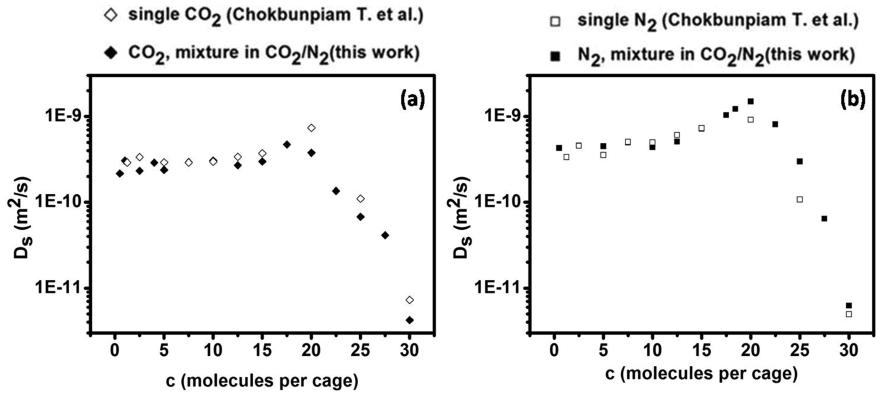

Figure 3. Molecular self-diffusion of CO_2 and N_2 at 300 K for the single-component loadings of 0.5−30 molecules/cage and the mixed gas loadings of 0.5 CO_2/0.5 N_2 to 15 CO_2/15 N_2 molecules/cage in ZIF-8 framework by MD simulations.

20 million simulation cycles. Higher densities needed a longer equilibration period. After equilibrium was established, the evaluation takes place during another 10−20 million simulation steps.

For the adsorption isotherms of the mixture at 298 and 273 K we did two kinds of equimolar simulations. In case A we kept the ratio of the numbers of guest molecules of the two molecular species CO_2 and N_2 as 1:1 constant in box A (gas box), but changed the gas box size, thus realizing different densities of guest molecules in the gas phase, which means different pressures. Because a change of the box size will normally affect this ratio, the particle numbers were then modified by trials in such a way that the ratio of the two guest molecule numbers was with a remaining difference of about 1% again 1:1 in box A for each case in the equilibrium state. From these equilibrated systems we then calculated the adsorption isotherms and the adsorption selectivity and the fugacities. In case B we modified for each gas volume the ratio of the two guest molecule numbers in box A by trials. After each trial the system had to relax in an equilibrating simulation run. Then the resulting ratio of the particle numbers in box B showed if additional trials and relaxations were necessary to obtain equimolar mixture in box B.

3. RESULTS AND DISCUSSION

3.1. Influence of the CO_2/N_2 Mixtures in ZIF-8 on the Window Size Found in MD Simulations. Figure 2 shows the change of the window size with the loading for mixtures of CO_2 and N_2. At low loadings (Figure 2a) the window sizes become slightly smaller from 3.375 to 3.195 Å. However, from 10 CO_2/10 N_2 to 15 CO_2/15 N_2 for equimolar adsorbed mixtures in ZIF-8 (Figure 2b) a gate opening up to more than 3.7 Å can be observed. For the adsorbed mixture of the composition CO_2/N_2 = 4:1 in ZIF-8 (Figure 2c) the gate opening starts at 16 CO_2/4 N_2.

Therefore, the window sizes from single-component gases CO_2, N_2, and CO_2/N_2 mixture adsorption can be ordered[17,20] CO_2 > CO_2/N_2 > N_2 (4.125 > 3.885 > 3.585). These results confirm that CO_2 has a much larger effect on the window size of the ZIF-8 framework than N_2.

Adsorbed N_2 and CO_2 as single-component gases at 298 K were shown by Chokbunpiam et al.[19,20] to lead to the gate opening at loadings of 18.44 and 22.5 molecules/cage, respectively. For the equimolar adsorbed mixture CO_2/N_2 in ZIF-8 gate opening was found at 10 CO_2/10 N_2, i.e., for 20 guest molecules/cage. Thus, gate opening is found for a mixed loading which is closer to the transition loading of pure N_2 than to that of pure CO_2. This can probably be explained in terms of the fugacities: a 4 times higher fugacity of N_2 than that of CO_2 is necessary to have an equimolar adsorbed mixture CO_2/N_2 as shown by GEMC at pressures up to 50 bar (see Figure 10). Assuming that also at higher pressures (not accessible for GEMC) the fugacity of N_2 is higher than that of CO_2, the dominance of N_2 is plausible. Interestingly, also for the 4:1 ratio CO_2/N_2 the gate opening starts at a total loading of about 20 guest molecules/cage. The fugacity of N_2 for the 1:1 ratio of CO_2/N_2 in the gas phase at pressures up to 50 bar is also higher than that of CO_2, and the difference increases more than linearly with the loading. But for total loadings of 20 molecules/cage the bulk free mixture outside of the ZIF cannot be examined by our GEMC as mentioned.

3.2. Diffusion Coefficients of the CO_2/N_2 Mixture in ZIF-8. The self-diffusion coefficients are shown in Figure 3. All self-diffusion coefficients D_s of CO_2 and N_2 as single-component gas as well as in the mixture CO_2/N_2 were found to be around 10^{-9} to 10^{-12} m^2/s and follow a similar trend. For the single-component gases, D_s did not change significantly at low loadings, but for loadings above 20.0 molecules/cage, respectively, in refs 19 and 20 the D_s values of N_2 and CO_2 drop dramatically down to 10^{-12} m^2/s. The same can be observed for the mixture. These results are interesting in connection with the transition structure and the change of the window size as a function of loading as shown in the above section. Obviously, with increasing loading of gas molecules in ZIF-8, the mutual blocking by molecular collisions has a stronger influence than the gate opening. Interestingly, the radial density functions (RDFs) do not indicate significant changes in the structure of the adsorbed mixture in comparison to single-component CO_2 adsorption. Such changes could be important for diffusion. From the RDFs reported here (for pure CO_2 see Figure S3 of the Supporting Information) and those of Chokbunpiam et al.[19] it follows that the maximum height of the first peak for C−C (means carbon atoms of two CO_2 molecules) is 3.2 in the pure gas simulation and 3.5 in the mixture. For C−O (means carbon atom of one and O atom of another CO_2 molecule) it is 2.0 in the pure gas simulation and 2.0 in the mixture. For O−O (means oxygen atoms of two CO_2 molecules) it is also 2.0 in the pure gas simulation and 2.0 in the mixture, and for N−N (means nitrogen atoms of two N_2 molecules) it is 2.0 in the pure gas simulation and 2.3 in the mixture. Significant differences that would indicate structural changes do not appear.

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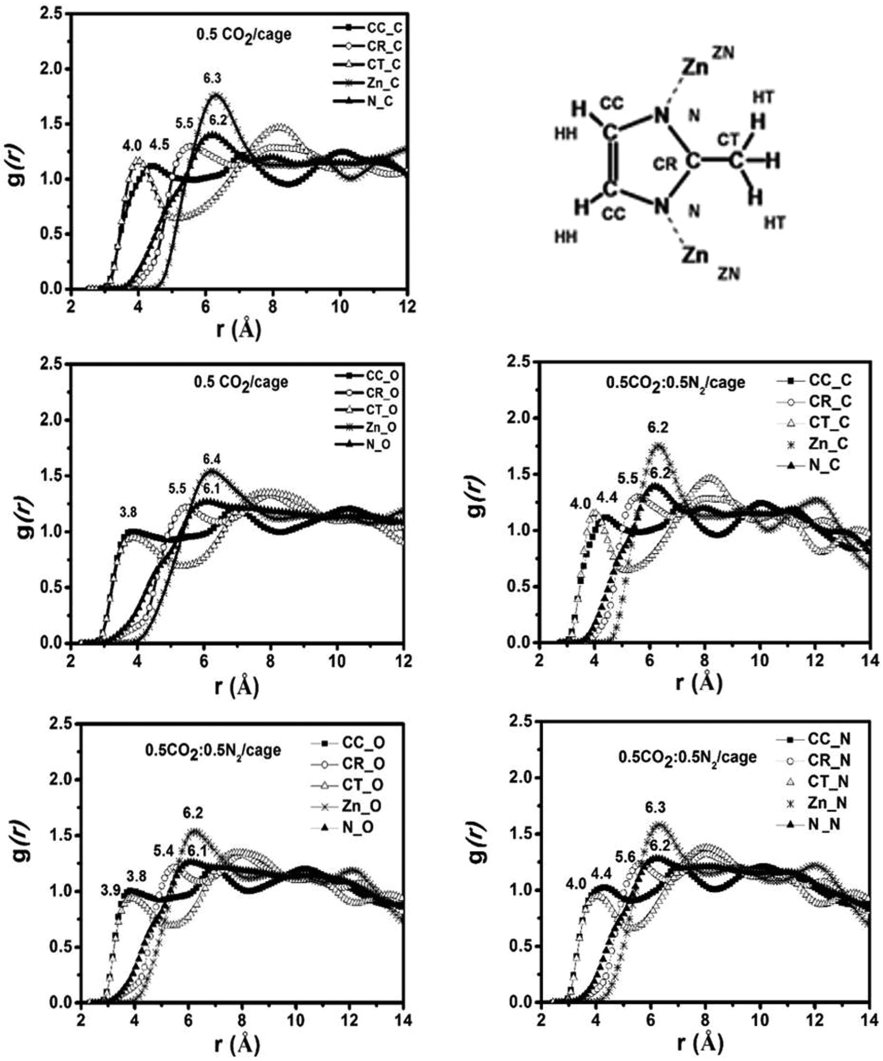

Figure 4. RDFs between atoms of guest molecules with lattice atoms in single-gas CO_2 and CO_2 and N_2 in the mixture 0.5 CO_2/0.5 N_2 in ZIF-8 at low loading.

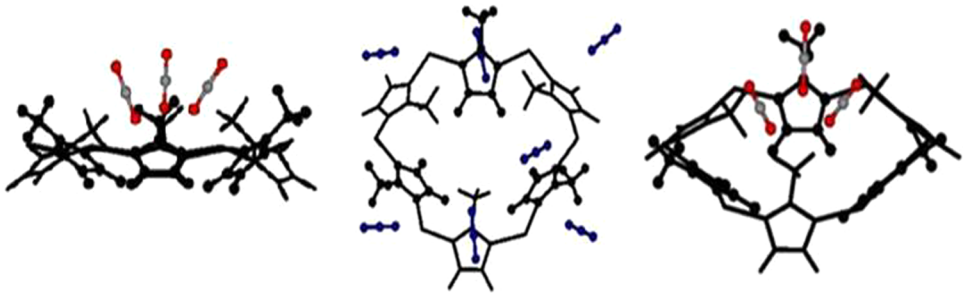

Figure 5. Favorite orientation of CO_2 at adsorption sites inside the ZIF-8 framework.

For the diffusion selectivity it can be seen that N_2 can diffuse a little bit faster than CO_2 at all loadings and temperatures. That means that N_2 can move within the ZIF-8 framework somewhat faster than CO_2 in the mixture of CO_2/N_2. For numerical values see Table S1 in the Supporting Information. The adsorption selectivity is discussed below.

3.3. Adsorption Sites of the CO_2/N_2 Mixture in ZIF-8.

In Figure 4 RDFs between atoms of CO_2 with lattice atoms in single-gas CO_2 and between atoms of CO_2 and N_2 in the mixture 0.5 CO_2/0.5 N_2 in ZIF-8 at low loading are given. It follows from Figure 4 that the favorite adsorption sites of single-gas CO_2 and mixed gas CO_2/N_2 are positions close to atoms of the organic linkers such as CC and CT (for the meaning of these abbreviations see the lattice fragment picture in Figure 4). Moreover, the carbon atom C of the CO_2 molecules as single gas as well as in the CO_2/N_2 mixture has a stronger interaction with the ZIF-8 framework than the O atoms of CO_2 and the N atoms of N_2. The RDFs of CC−C and CT−C show sharper peaks than CC−O, CT−O, CC−N, and CT−N.

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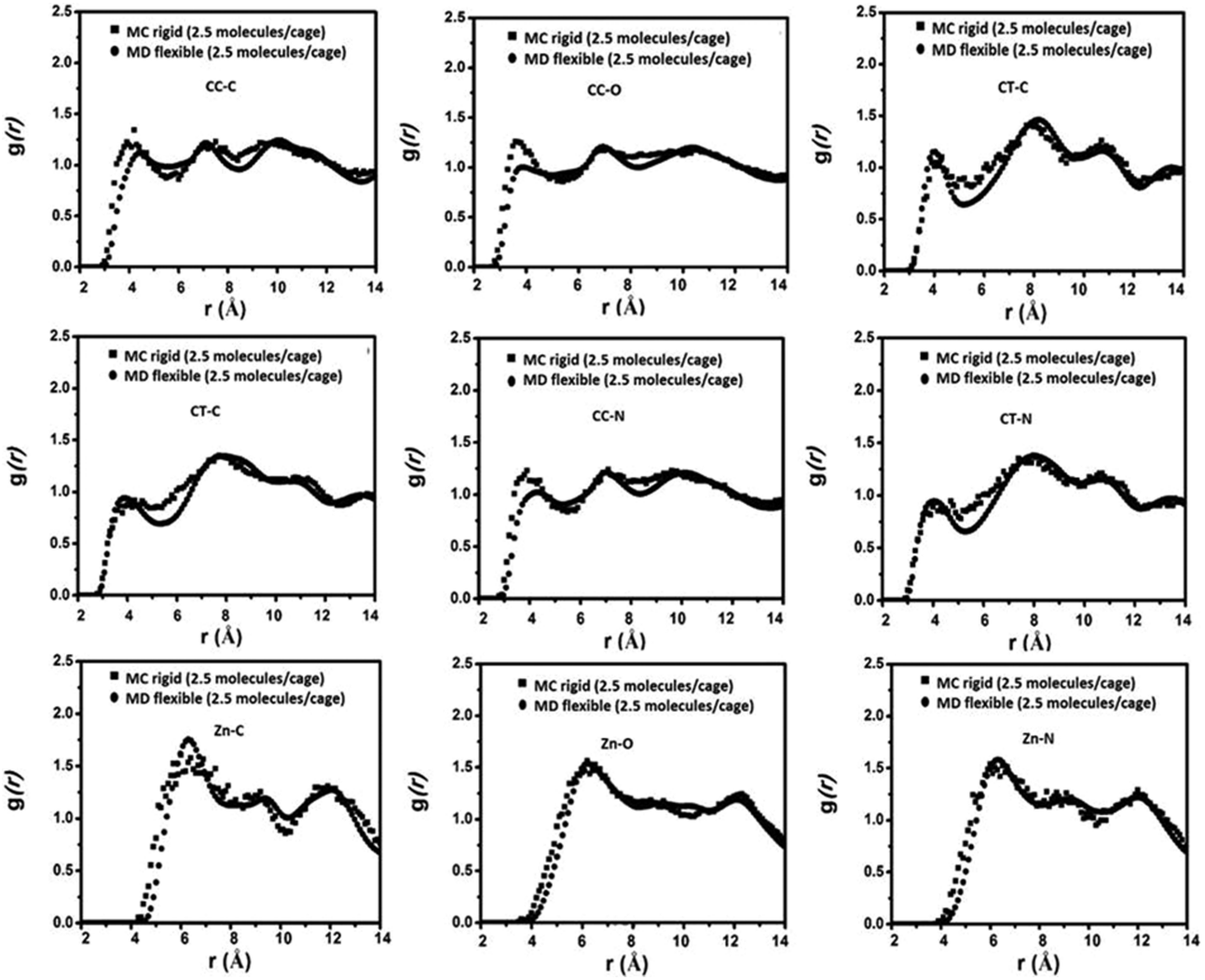

Figure 6. Comparison of the RDF graphs of ZIF-8 (CC, CT, and Zn) and guest molecules (C, O of CO_2 and N of N_2) from flexible MD and rigid MC.

Additional RDF graphs among all atom types of guest molecules and some RDFs with the ZIF-8 lattice are shown in Figures S1−S4 of the Supporting Information. All RDF results support our interpretation.

The main orientations of guest molecules were parallel with CC and CT of the framework as shown in Figure 5.

The RDFs for CO_2/N_2 mixtures at different loading are shown in the Supporting Information. The results give clear evidence for preferential sites and the gate-opening effect because $g(r)$ of guest molecules still remains nearest at CC and CT positions. With increasing loading of guest molecules, sharp peaks are seen around CC, CT, and Zn. Thus, the strong interaction between CO_2 and N_2 with the organic linker at high loading as shown in the RDF can be important for the rotation of the linker.

3.4. Comparison of the RDF from Flexible MD and Rigid MC. For an additional check of the equivalence of flexible MD and rigid MC, the RDFs between the C atom of CO_2 and the lattice CC and the O atom of CO_2 and the lattice CC resulting from the two different simulation methods are compared for the CO_2/N_2 mixture at a loading of 2.5 molecules/cage. The RDF graphs between ZIF-8 (CC, CT, and Zn) and guest molecules (C, O of CO_2 and N of N_2) are shown in Figure 6. These graphs confirm that the structure of the adsorbed phase is found to be similar in flexible MD and rigid MC.

3.5. Adsorption Isotherm of Pure N_2 from GEMC. Figure 7 shows a comparison of the adsorption isotherm for N_2 which is the result of our GEMC simulations employing the

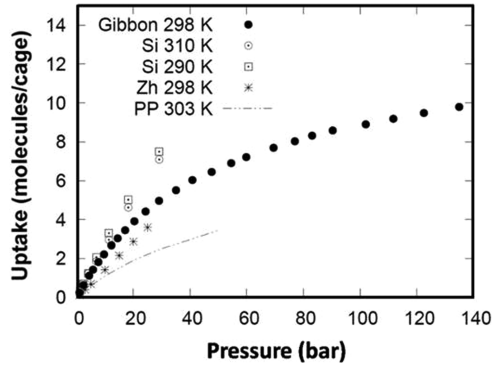

Figure 7. Adsorption isotherms for pure N_2 on ZIF-8. Si means Simmons et al. (ref 24), Zh means Zhang et al. (ref 31), and PP means Pérez-Pellitero et al. (ref 23).

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interaction parameters that were also used in the MD simulations of the present paper (full dots), with former combined experimental and simulation results. Two isotherms of Simmons et al.[24] obtained at 290 and 310 K show both larger values, whereas the values of Zhang et al.[31] and Pérez-Pellitero et al.[23] are smaller than the values of the present simulations.

3.6. Adsorption Behavior of the Equimolar Mixture CO_2/N_2 from GEMC. From the low-pressure region of adsorption isotherms published in different papers values of the adsorption constant K as defined in eq 1 for N_2 and CO_2 in ZIF-8 are extracted. They are compared in Table 1 with corresponding values from our simulations, using the Gibbon software.

The low-pressure results of Simmons[24] for N_2 at 290 K and at 310 K practically agree with each other and have therefore been used here for the comparison with our 298 K results. Note that, in the case of the mixture, the adsorption constant K has been defined via the partial pressure, not via the total pressure. For the equimolar mixture, the partial pressures at low density are simply half of the total pressure. In the limit of vanishing pressure, the mixture can be regarded as ideal gas and ideal mixture.

From Table 1 it can be seen that large differences between the experimental adsorption results from different papers exist (as stated already by Chokbunpiam et al. for CO_2 in ref 20) and that the Gibbon results using our parameter set, as described above, are near the mean of the scattering experimental values. The values from Zhang et al.[31] that are shown in Table 1 are averaged over the interval 1−5 bar. The reason is that for very low pressures (<1 bar) the isotherm for pure N_2 given in paper 31 shows a strongly nonlinear behavior (see Figure 1 in ref 31). On the contrary, in the range of 1−5 bar (see Figure 6a in ref 31) the uptake seems to be proportional to the pressure like in all other mentioned papers and like in our simulation results for the interval 0 bar < p < 5 bar. Note that the mixture results of refs 21 and 31 that we used to calculate K in Table 1 have not been measured or simulated, but they are calculated from pure species data by IAST.

Adsorption isotherms at different temperatures for pure CO_2 have been given by Chokbunpiam et al.[20] They have been calculated using the same parameters for CO_2 and the lattice atoms that are employed in the present paper.

Figure 8 shows the adsorption isotherms for mixtures CO_2/N_2 at 298 K and at 273 K. Case A means equimolar in the gas phase corresponding to a ratio 4:1 at 298 K and 5:1 at 273 K in the adsorbed phase. Case B corresponds to equimolar mixture in the adsorbed phase corresponding to a ratio 1:4 at 298 K and 1:5 at 273 K in the gas phase. In case B, the almost equimolar mixture in the adsorbed phase is constructed by trial variations of the CO_2/N_2 ratio in the gas phase. The results can be seen in Figure 8. Interestingly, in case A the adsorption of N_2 in this mixture is not much influenced by the temperature change, while the adsorption of CO_2 is enhanced by about 25% by decreasing the temperature from 298 to 273 K. The resulting CO_2/N_2 adsorption selectivities S_a can be seen in Figure 9. It

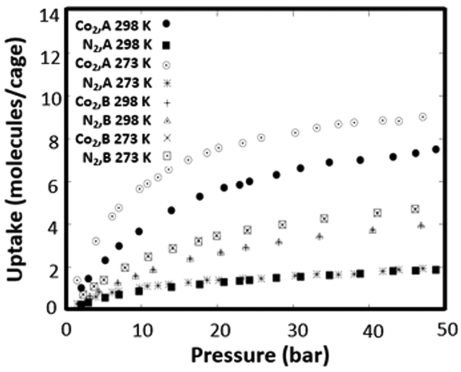

Figure 8. Adsorption isotherms for equimolar mixtures CO_2/N_2. A means equimolar in the gas phase and B means equimolar in the adsorbed phase.

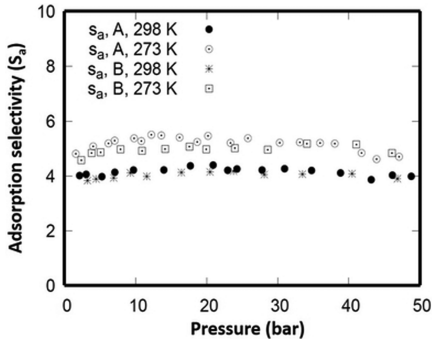

Figure 9. Adsorption selectivity CO_2/N_2 as a function of the gas-phase pressure for equimolar mixtures CO_2/N_2. A means equimolar in the gas phase and B means equimolar in the adsorbed phase.

turns out that the selectivity at 273 K is about 5 and at 298 K it is about 4, while the influence of the loading and also of the ratio of the species in the gas phase does not much influence the selectivity.

In Figure 9 of McEwen et al.,[21] the adsorption selectivity CO_2/N_2 at 298 K and 1 bar as calculated by IAST from pure species adsorption isotherms is given. The adsorption selectivity is low and does not depend upon the CO_2/N_2 ratio. However, the exact value of the adsorption selectivity is difficult to derive from Figure 9 of ref 21 because of its relatively small value for ZIF-8. The estimated adsorption selectivity in McEwen et al.[21] is of the order of our value, but it seems to be somewhat larger. This is clearly due to the stronger adsorption of N_2 in our model (see Table 1).

In McEwen et al.,[21] the adsorption selectivity CO_2/N_2 at 298 K is calculated from pure component adsorption data by IAST as a function of the pressure. A slight decrease of the selectivity with increasing pressure has been found. The average value of the selectivity agrees well with our value. Neither in Zhang et al.[31] nor in McEwen et al.[21] have mixture simulations been carried out.

The CO_2/N_2 adsorption selectivity depends much more on the temperature than on the pressure. For both temperatures it seems to be slightly higher for densities around 4×10^{-4} molecules per Å^3 than for the other densities, but this difference is still too close to the magnitude of the fluctuations to be sure.

We also calculated a predicted membrane selectivity as proposed in refs 9 and 43−45

$$\alpha_{ij}^{\text{membrane}} = (\alpha_{ij}^{\text{diffusion}})(\alpha_{ij}^{\text{adsorption}})$$

with the diffusion selectivity $\alpha_{ij}^{\text{diffusion}}$ as the ratio of the self-diffusivities of the species i and j and the adsorption selectivity $\alpha_{ij}^{\text{adsorption}}$ as the ratio of the adsorbed amounts of i and j.

We investigated at 298 K the mixture equimolar in ZIF-8 at concentrations of 1.25 and 2.5 guest molecules per cage. These

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are the two low-pressure cases in Table S1 of the Supporting Information for which we can do GEMC simulations. For 1.25 molecules per cage (at the pressure of 3.2 bar) we find an adsorption selectivity

$$\alpha_{ij}^{\text{adsorption}} = 3.84$$

with i meaning CO_2 and j meaning N_2. With the diffusion selectivity (see Table S1 in the Supporting Information)

$$\alpha_{ij}^{\text{diffusion}} = 0.865$$

we find the membrane selectivity $\alpha_{ij}^{\text{membrane}} = (\alpha_{ij}^{\text{diffusion}})\text{-}(\alpha_{ij}^{\text{adsorption}}) = 0.865 \times 3.84 = 3.32$. This value is lower than the value 5.72 found by Pusch et al.[33] in the low-pressure limit but closer to the results of Diestel et al.[46] who found in mixed gas permeation on a supported ZIF-8 membrane a separation factor $CO_2/N_2 \approx 2$ from mixed gas permeation studies.

For 2.5 molecules per cage that corresponds to a pressure of 6.88 bar we find an adsorption selectivity of

$$\alpha_{ij}^{\text{adsorption}} = 3.93$$

With an diffusion selectivity (from Table S1) of

$$\alpha_{ij}^{\text{diffusion}} = 0.742$$

we find the membrane selectivity to be $\alpha_{ij}^{\text{membrane}} = 2.92$. This is in acceptable agreement with results of Diestel et al.[46] who found the membrane selectivity ≈2 as mentioned above.

Figure 10 shows the fugacities of CO_2 and N_2 at 298 K and at 273 K as a function of the gas-phase pressure for both cases A and B of the equimolar mixtures CO_2/N_2. These fugacities are calculated by use of the Peng–Robinson equation[42] for a mixture from the gas-phase densities and the temperature, respectively. For each species the fugacity in the gas phase and in the adsorbed phase is equal in equilibrium. Hence, the GEMC simulation again provides the possibility to calculate thermodynamic quantities for the adsorbed species easily from the gas phase. The fugacity, that at low pressure agrees with the partial pressure for each species, can help to discuss the thermodynamic impact of each species on the lattice. In case B, in which the mixture is equimolar in the adsorbed phase, the fugacity of N_2 is much larger than that of CO_2. That means much higher fugacity is necessary to press the same amount of nitrogen into the pores. This high fugacity that is similar to a kind of partial pressure can explain that the gate opening in case B is dominated by N_2 if we assume that also at the high loadings where gate opening happens (and that cannot be realized in our GEMC) the fugacity of N_2 is still larger than that of CO_2. Also in case A, although the mixture in the gas phase is equimolar, the fugacities agree only up to about 10 bar, while for higher pressure the fugacity of CO_2 increases more slowly. The difference increases stronger then linearly.

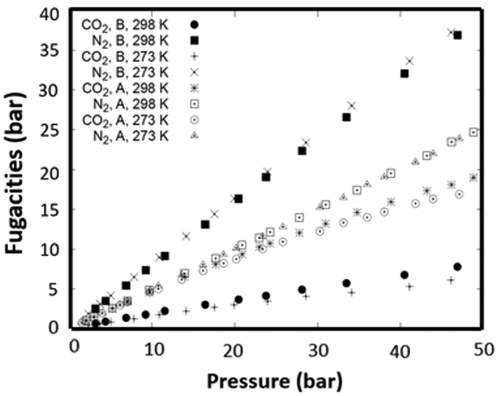

Figure 10. Fugacities of CO_2 and N_2 at 298 K and at 273 K as a function of the gas-phase pressure for equimolar mixtures CO_2/N_2. A means equimolar in the gas phase and B means equimolar in the adsorbed phase.

4. CONCLUSIONS

Molecular adsorption and diffusion of the gas mixture N_2/CO_2 in the metal–organic framework ZIF-8 are investigated by using MD and GEMC simulations. The validation of the interaction parameters by comparison with experimental adsorption results shows satisfactory agreement.

While the adsorption of N_2 was found to be in a temperature window from 298 to 273 K almost independent of the temperature, the adsorption of CO_2 shows the clear van't Hoff dependence and decreases with increasing temperature, which results in an increasing CO_2/N_2 adsorption selectivity with decreasing temperature.

Gate-opening effects as investigated before for single-component gas adsorption could also be observed for the CO_2/N_2 mixture in ZIF-8. In the mixture CO_2/N_2, gate opening of ZIF-8 happens at a total amount adsorbed of 20 molecules/cage, while for single-component CO_2 it happened at 22.5 molecules per cage and for pure N_2 at 18.4 molecules per cage. The stronger influence of N_2 on the start of gate opening can be understood in terms of the fugacity of N_2 that has been found in GEMC for all pressures up to 50 bar for the equimolar mixture in ZIF-8 to be 4 times larger than that of CO_2. Note, however, that the gate opening was found at larger pressure that cannot be investigated by GEMC as mentioned. Evaluation of the self-diffusion coefficient and diffusion selectivity from MD and adsorption selectivity from GEMC made it possible to calculate membrane selectivities that agree satisfactorily with experiments.

The strong decrease of the self-diffusion coefficient at high loadings, due to the mutual hindrance of the guest molecules at high occupancy, happened in the mixture at about the same total loadings of guest molecules in comparison to single-gas loadings. Obviously the influence of the mutual hindrance could not be compensated by the gate opening.

Investigations of the structure by RDFs of the adsorbed guest molecules do not show remarkable differences to the structure of adsorbed pure CO_2. Favorite adsorption sites of all guest molecules in single-gas CO_2 and mixed gas CO_2/N_2 are positions close to atoms of the organic linkers.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b05506.

Details of the radial distribution functions, self diffusion coefficients, and diffusion selectivities (PDF)

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Notes

The authors declare no competing financial interest.

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Methane in zeolitic imidazolate framework ZIF-90: Adsorption and diffusion by molecular dynamics and Gibbs ensemble Monte Carlo

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CH4 in ZIF-90

ABSTRACT

There is experimental evidence from adsorption and permeation studies that methane can enter the Zeolitic Imidazolate Framework (ZIF)-90 framework despite the fact that the critical diameter of methane (3.8 Å) is larger than the window size of ZIF-90 (3.5 Å) assuming a rigid framework. Therefore, adsorption and diffusion of methane in the ZIF-90 were investigated by Molecular Dynamics (MD) and Gibbs Ensemble Monte Carlo. Various interaction force fields have been tested and a suitable one has been proposed. Results of structural and dynamical properties of methane in ZIF-90 are presented. Like for methane in ZIF-8, no gate opening was found in this paper for methane in ZIF-90 up to a pressure of 260 bar. Therefore, the adsorption and diffusion of methane in ZIF-90 can be explained by a flexible framework.

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1. Introduction

During the last decades, new porous materials, called Metal-Organic Frameworks (MOFs) a sub-class of coordination polymers [1] have been found as promising candidates for many industrial applications because of their intrinsic properties like large surface area and pore volume, big variety of structures and adjustable pore size. Zeolitic Imidazolate Frameworks (ZIFs) being a subclass of MOFs have attracted the most attention from scientists due to their – for MOFs – relative high thermal and chemical stability [2]. Among over 150 different ZIFs [3], ZIF-8 and ZIF-90 are investigated by many scientists, especially for gas separation because of their average window size that is close to the size of technically important molecules (CH_4, N_2, CO_2 and others). In ZIF-90, the Zn^{2+} ions are interconnected by imidazolate-carboxyaldehyde anions to a SOD structure with a pore size of 3.5 Å [4] which is between the molecular size of CO_2 (3.3 Å) and CH_4 (3.8 Å). This pore size of 3.5 Å recommends ZIF-90 as a candidate for the separation of CO_2 from bio or natural gas by molecular sieving. Further, the aldehyde group of the ZIF-90 linker interacts additionally with CO_2 [5]. However, in adsorption studies also small alcohols with a critical diameter >4 Å could be adsorbed on ZIF-90 [6] and methane easily permeates through ZIF-90 membranes [7–10].

While adsorption and diffusion of guests in ZIF-8 have been widely studied by different theoretical methods, for ZIF-90 only a few theoretical studies seem to exist.

Atci and Keskin [11] have simulated the adsorption and diffusion of various gases in ZIF-90 and other ZIFs thus evaluating the separation potential of different ZIFs. Hence, they used the rigid model for all frameworks with the UFF force field of non-bonded interactions. Thornton et al. [12] performed the first simulations on flexible framework of ZIF-90, however, they focused mainly on ZIF-

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11 and they modified the DREIDING force field to obtain the adsorption isotherms of ZIF-11. Furthermore, the lack of the charges in their model strongly affects the simulations of non-spherical molecules like CO_2 or N_2 with partial charges that result in quadrupole moments. Gee et al. [6] performed in a pioneering paper examinations of the diffusion and adsorption of small alcohols in ZIF-90 in both rigid and flexible models, in which the interactions were described by GAFF and DREIDING force fields. The results showed a significant effect between rigid and flexible framework in the self-diffusion coefficient (D_s) and the flexible model using GAFF gives better results compared with the experiment. This influence of the flexibility on D_s can also be found in other ZIFs [13–15] and MOFs [16] while the adsorption isotherm seems to be much less sensitive with respect to the lattice flexibility [17,18] as long as no structural phase transition like the so called gate opening [19–21] takes place. On the other hand, Zhang et al. [22] found that the DREIDING force field produced better results than GAFF in terms of the adsorption isotherm. Therefore, the choice of interaction parameters for rigid and flexible models in terms of adsorption isotherms and D_s and the effect of the gas molecule concentration on the ZIF's structure are still questionable.

Methane is the main component of natural gas and of biogas. Before methane is used in many industrial processes and energetically in households and industry, it has to be concentrated, usually CO_2 and N_2 have to be separated by using different technologies. Adsorption or permeation using ZIF-90 adsorbents or membranes, respectively, could become novel options. Although having a bigger diameter (3.8 Å) compared with the window size of some ZIFs like ZIF-8 (3.4 Å) and ZIF-90 (3.5 Å) [2,4], methane can diffuse within these frameworks.

In this work, structural properties like density distributions and radial distribution functions (RDF's) as well as adsorption and self-diffusion of methane molecules in ZIF-90 are examined by both Molecular Dynamics (MD) and Gibbs Ensemble Monte Carlo (GEMC) simulations. Studying diffusion and adsorption of methane in ZIF-90 shows the influence of the framework flexibility on these properties. But also a possible influence of the adsorbed molecules on the lattice structure *e.g.* gate opening as found in Refs. [16,19,21] for other MOF's and ZIF's and guest molecules can be checked. In addition, a better understanding on the atomic level of the adsorption isotherm, diffusion mechanisms, or adsorption sites can be achieved.

Unfortunately, there is still much uncertainty about the choice of parameters to be used in such simulations. Hence, first the existing force fields must be carefully examined and evaluated. Therefore, in this work, various parameters for the ZIF-90 lattice and for methane molecules from the literature will be tested and compared for rigid and flexible models. The results obtained in this way will hopefully provide parameters yielding good agreement with experiments in terms of adsorption isotherms, X-ray structure and dynamical properties.

2. Simulation details

2.1. Model and force field parameters

The structure of the ZIF-90 framework was obtained from the Cambridge Crystallographic Data Centre (CCDC), determined by Morris et al. [4]. The simulation box consists of $2 \times 2 \times 2$ unit cells in the Molecular Dynamics (MD) simulation and $4 \times 4 \times 4$ unit cells in the Gibbs Ensemble Monte Carlo (GEMC) simulation. The diffusion of methane molecules can only proceed through the 6-membered rings that connect adjacent cavities. They are called 'windows' in the following. Other connections between the cavities are too small to allow the passage of methane molecules.

From a literature review [6,21,23] we found that the most common force fields for the framework that could produce a stable lattice size and dynamical properties were that of GAFF (which is a generalized AMBER force field) [6] and that of DREIDING [6]. Therefore, GAFF and DREIDING as well as modifications of them were tested in this work to describe both the bonded interactions (bond, angle, torsion and dihedral) and the non-bonded interactions (van der Waals interactions).

The charges of atoms, collected in Table 1, were calculated by the DDEC method [6] and then slightly modified in order to neutralize the system as documented in Table 1.

In addition, we tested five different force fields of CH4 for their ability to reproduce the adsorption behavior of CH4 in ZIF-90. The corresponding parameters are shown in Table 2. In Ref. [15] the parameters for methane have been taken from the Transferable Potentials for Phase Equilibria Force Field (TraPPE) of M.G. Martin, J.I. Siepmann, J. Phys. Chem. B. 102 (1998) 2569–2577. Parameters that have been developed for adsorption of guest molecules [24], in zeolites [25], in ZIF-95 [26], in Covalent Organic Frameworks have been taken from these papers. The parameters of [27] have been used for structure investigations of methane in the gas phase. CH4 was treated as a spherical molecule in the force fields 1 (FF1) to 4 (FF4) and as a flexible molecule model containing 5-interaction centers in the force field 5 (FF5).

2.2. Gibbs Ensemble Monte Carlo simulations (GEMC)

For the GEMC simulations, the home made simulation software 'Gibbon' was used like done before in Refs. [17,19]. A combination of GEMC and MD by DL_POLY was also applied in Ref. [18] where the different lattice structures for lower and higher pressures as obtained from flexible lattice MD were used for GEMC simulations. In contrary, in Refs. [17,19] the GEMC has been carried out only in pressure regions where no structural phase transition could be found in the corresponding MD. Hence, only one structure was of interest.

In GEMC two simulation boxes were set up, box A and box B. Box A contained guest molecules (CH_4) in bulk free gas, and box B represented $4 \times 4 \times 4$ unit cells of the ZIF-90 framework with adsorbed methane guest molecules. At low pressure of 0–1 bar, the system was run 10^5 steps until equilibrium could be stated by observing stable uptake in box B and agreement of the chemical potentials in both boxes. Then an evaluation part of 10^6 steps was started. At higher pressure (up to 255 bar), 10^6 steps were necessary to approach to equilibrium and the evaluation part was then 10^7 steps. The adsorption simulation runs started from random situations sometimes with initial flux from gas phase to adsorbed phase, sometimes in opposite direction. The results fitted well together. Searching hysteresis effects was not the subject of this paper and would have needed larger initial deviations from the equilibrium.

Table 1
Partial charges of the atoms in the ZIF-90 framework.

Atom type	Charge (Gee et al. [6])	Adjusted charge
C_CR	0.2104	0.21
C_CC	−0.0001	−0.002
C_CT	0.2582	0.258
H_H4	0.1149	0.115
H_HT	0.0476	0.049
Zn	0.6726	0.674
O	−0.4091	−0.41
N	−0.332	−0.335
Total charge of the lattice	1.728	0

Table 2
Force fields for methane.

Source	Molecules	ε(K)	σ(Å)	Charge
FF1 [24]	CH_4	158.5	3.72	0
FF2 [15]	CH_4	147.9	3.73	0
FF3 [25]	CH_4	173.2	3.8842	0
FF4 [26]	CH_4	191.235	3.71	0
FF5 [27]	$C(CH_4)$	30.7	3.74	−0.24
	$H(CH_4)$	14.1	2.67	0.06

The temperature was chosen to be 303 K for a comparison with the experimental data of [28] for testing the force fields. But the temperature was set 300 K for studying other system properties corresponding to the results in MD simulations.

Using the Gibbon software for GEMC simulations, in each simulation step there is first a random decision if a trial of a shift or rotation of a randomly chosen molecule in box A or box B takes place, or if a particle is tried to be swapped from one box to the other one. If a swap is to be tried then according to [29] first one of all particles is chosen randomly, no matter in which box it is, and then a trial to swap it is accepted or not with the proper probability given in Ref. [29]. This will lead to an equilibrium between the gas phase and the adsorbed molecules.

In Gibbon the Coulomb interactions are not calculated by the computer time expensive method of Ewald summation. First in Ref. [30] it has been shown that in many particle systems, which are neutral in sum of the charges, for large distances Coulomb interactions are reduced by many-particle effects and can be dropped down by shifted forces or similar models. This technique has meanwhile been used in many papers *e.g.* in Refs. [19,31]. In the Gibbon software the Coulomb interactions are dropped down smoothly at a cutoff distance of 30 Å. The box size used in GEMC is 69.086 Å. We made tests that showed that the efficiency of this method can be strongly improved by a simple trick: Doing the cutoff molecule by molecule not charge by charge. The procedure is described in the supporting information.

The cutoff for the van-der-Waals forces (Lennard-Jones) has been chosen to be 14 Å like in the MD simulations.

While in Grand Canonical Monte Carlo (GCMC) simulations the loading of the ZIF with guest molecules is found as a function of the chemical potential, GEMC provides the exact information about which gas phase density outside of the ZIF corresponds to a given loading of the ZIF with guest molecules.

Hence, in the GEMC simulations the pressure can be evaluated in the gas phase while this would be ambiguous within the ZIF crystal. On the other hand, the chemical potential for comparison is usually not available from adsorption experiments while the corresponding gas phase density is usually known.

The pressure in the gas phase can be calculated directly from the virial theorem or from an equation of state based on the density of particles. The Peng-Robinson equation of state [32] was chosen in this work to calculate the pressure. Thus, the amount of guest molecules adsorbed in ZIF-90 could be estimated as a function of the gas phase pressure.

During GEMC simulation, ZIF-90 was assumed to be rigid because previous papers about guest molecules adsorbed in ZIF's showed that the effect of the lattice flexibility on adsorption was not significant [17,18]. In this work, GEMC served as a touch-stone for a reasonable force field for ZIF-90 and as a tool to examine static properties of the adsorbed guest molecules like radial density functions (RDF's) *etc*. It was interesting to compare RDF's from GEMC with rigid lattice with those of MD with flexible lattice in order to check the reliability of the rigid model for static properties.

2.3. Molecular Dynamics simulations (MD)

The force fields which gave good results for the adsorption isotherm were used to study also dynamical properties and the structure of ZIF-90 in MD simulations. From previous work [13–16] it is known that dynamical properties like the self-diffusion coefficient of guest molecules in many different ZIFs strongly depend on the flexibility of the framework. In this work, the MD simulation was conducted on both rigid and flexible frameworks to compare the results and find out the importance of the structure flexibility of ZIF-90 for methane as guest. All MD simulations in this work were run by DL_POLY 2.20 [33].

Our MD runs are mainly done in the NVE ensemble in which the size of the MD box is fixed to a size that fits to the ZIF-90 crystal dimensions from the database, also with flexible lattice. But, in order to check the consistency of the bonded parameters of the elastic lattice, it is common use to let the size of box and lattice relax in NPT simulations. Therefore, we also did such additional tests before we used NVE for the other evaluations. The main reason why we prefer the NVE ensemble for our main investigations is the inaccuracy of the pressure calculations by the virial formula that are inherent in the NPT simulations.

First the box length of the MD simulation box containing $2 \times 2 \times 2$ unit cells (34.543 Å) was checked in isothermal-isobaric (NPT) ensemble MD for the flexible framework as a first test of the interaction parameters. For this purpose the NPT simulations were carried out for 1 ns to relax the system to equilibrium and then additional 2 ns served to collect data which were then compared with the experimental values of the size of the lattice and of the windows connecting adjacent cavities. The cutoff for van der Waals forces was 14 Å.

The dynamical properties were observed from micro-canonical ensemble Molecular Dynamics (NVE-MD). In these simulations the box size is constant per definition and has exactly the value given in the database from experiment. But, in the flexible lattice each of the 8 unit cells can still fluctuate in size and, more important for diffusion, also the size of the windows connecting adjacent cavities will fluctuate. The average value of the window size should agree with the value from the structure database.

First, to control the temperature of the system, isochoric-isothermal ensemble (NVT) MD simulation was conducted for 5 ns After that, the system was allowed to equilibrate for 0.5 ns and then the dynamical properties were examined during 10 ns in the NVE ensemble.

The window size distribution and the self-diffusion coefficient can be evaluated from the trajectories of these runs. Loadings of 0.5, 2.5, 10 and 15 CH_4 molecules/cage inside ZIF-90 were examined. In the NVE - MD runs the temperature was slightly fluctuating around a stable average value for each run that was close to 300 K, respectively.

The results were compared with available experiments and they were used to study adsorption sites and self-diffusion coefficients as well as the membrane permeance (see Fig. 1).

3. Results and discussion

3.1. Test of different force fields for the simulation of adsorption isotherm and the structure of ZIF-90

GAFF and DREIDING (DREID.) force fields for the framework and five different force fields of methane were applied to calculate adsorption isotherms at low pressure and 303 K by GEMC and to compare the results with experiments. The results are shown in Fig. 2a. At these low pressures the ideal gas formula is used for the

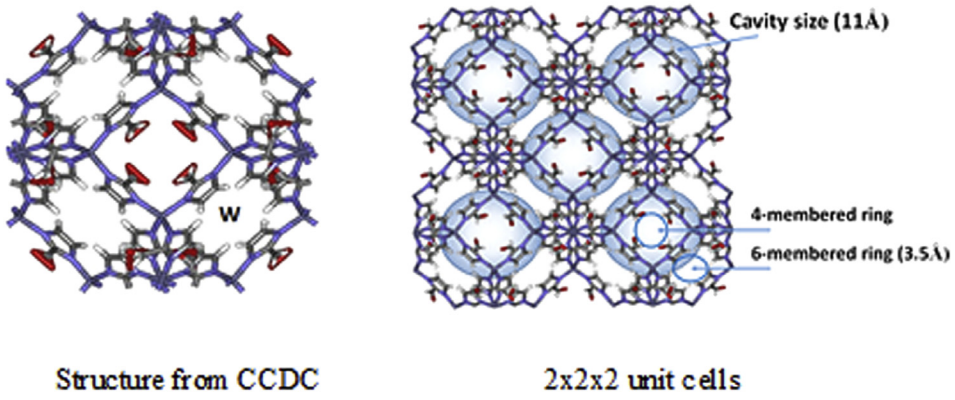

Fig. 1. Structure of ZIF-90. The 6-membered ring is called 'window' (w in the left part of the picture).

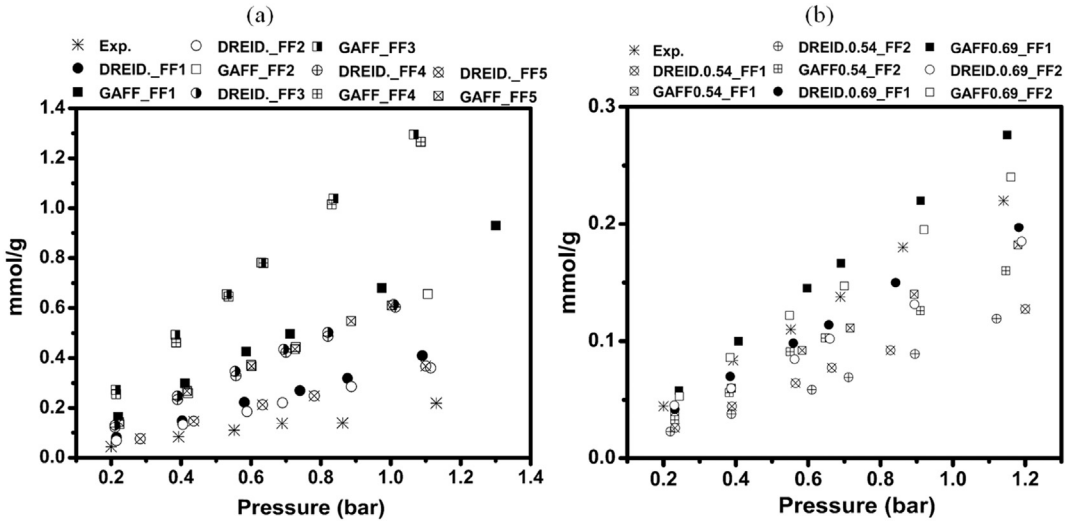

Fig. 2. a) Comparison of adsorption isotherms of five force fields for CH_4 (FF1-FF5) in ZIF-90 (GAFF and DREID.) at 303 K, b) the adsorption isotherm of CH_4 in ZIF-90 at 303 K after scaling the force field of the framework. Experimental data from Venkatasubramanian et al. [28].

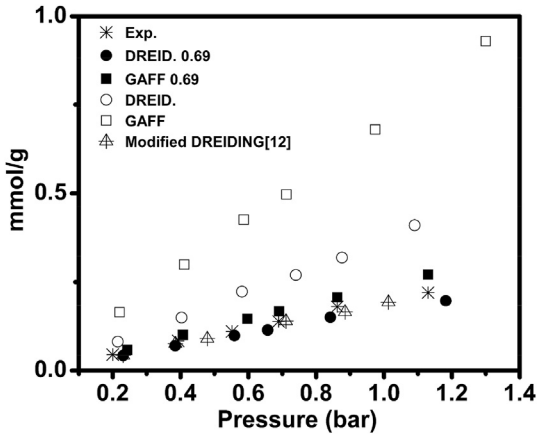

Fig. 3. Adsorption isotherm of CH_4 in ZIF-90 at 303 K for low pressure (0–1.2 bar) obtained from GEMC for the force field with and without modification. Experimental data from Venkatasubramanian et al. [28].

pressure calculations and thus the different molecular models do not have influence on the pressure calculations (see Fig. 3).

Note: The adsorption experiments [28] have been done at 303 K, therefore, we did GEMC simulations also at 303 K for comparison to test our parameters. These parameters have then been used for our MD simulations at 300 K. We carried out additionally tests at 303 K that showed that the MD results for both temperatures agreed within the range of fluctuations.

Fig. 2a shows that there is no force field which can produce the adsorption isotherm well. This is clearly due to the fact that the contribution of the van der Waal attraction to adsorption is overestimated. This overestimation was also found in other previous papers for water and alcohol adsorption in ZIF-90 [6,11]. Hence, the well-depth was scaled by the scaling factor obtained from Pérez-Pellitero et al. [23] $\varepsilon^* = 0.69\varepsilon$, $\sigma^* = \sigma$ and Zhang et al. [21] $\varepsilon^* = 0.54\varepsilon$, $\sigma^* = \sigma$ for both GAFF and DREIDING force fields. We call GAFF scaling 0.69 (GAFF 0.69), GAFF scaling 0.54 (GAFF 0.54), DREIDING scaling 0.69 (DREID. 0.69), DREIDING scaling 0.54 (DREID. 0.54) (see Table T1 in supporting information). We performed that scaling with only two popular force fields of guest molecules (FF1 and FF2) because these two force fields of methane have shown a good performance in many previous publications [11,12,15,23,24]. The adsorption isotherms obtained after modifying the force fields are shown in Fig. 2b.

It can be seen from Fig. 2b, that the modified GAFF (GAFF 0.69) and the modified DREIDING (DREID. 0.69) force fields can produce

better results for adsorption isotherms when they were compared with the others. Therefore, GAFF 0.69 and DREID. 0.69 force fields were chosen to further study of the structure and dynamical properties. Moreover, the GAFF force field can produce the lattice constant better than the DREIDING force field mentioned in the previous work [6]. So that to compare the effect of the scaling factor on the structure of the ZIF and its dynamical properties, GAFF was studied in this work.

On the other hand, GEMC was also conducted to evaluate adsorption isotherms with the force field developed by Thornton et al. [12]. In their work, they modified DREIDING to get a good adsorption isotherm of a series of ZIFs from Grand Canonical Monte Carlo ensemble (GCMC) by using a parameterization algorithm developed by Dubbeldam et al. [34]. Because they focused mainly on ZIF-11, the structure as well as the dynamical properties of ZIF-90 was not mentioned clearly. In this work, we found by GEMC with modified DREIDING also good agreement with the experiment. These results also show good agreement between the two methods GEMC and GCMC simulations for the adsorption isotherm as it has been expected.

For examining the dynamical properties, in this paper the NVE ensemble MD has been used because the calculation of the pressure (that is essential for NPT simulations) *e.g.* by the virial theorem for molecules in pores, particularly in the high pressure region is questionable. For example the cutoff correction to the virial result is well defined for gases and liquids but not for the molecules in pores. The importance of this correction increases in gases and liquids with the square of the density. Moreover, the scaling of intermolecular distances but, not of intramolecular distances, as usually done in NPT simulations, is questionable. In contrary, in NVE all quantities are well defined and the simulation box size corresponds to the structure of the database by definition. Nonetheless, the sizes of the different unit cells included in the MD box can still fluctuate. The most important structural feature for diffusion is the window size, controlling the migration of particles that must be reproduced well by the flexible lattice.

Nevertheless, as one property of the parameter sets, we additionally checked, which box size they would yield in NPT simulations, just as an additional information.

The distribution of the box length in NPT was shown in Fig. S2 and Table T2 in the supporting information gathering together the results from GAFF, GAFF 0.69 and DREID. 0.69 force field model and experiment. It can be seen from Table T2 that while GAFF and GAFF 0.69 force fields can hold a box length fitting with the XRD structure, the box length from DREID. 0.69 collapsed. The same results have been found in Gee et al. [6]. In addition, the window size was studied by analyzing results from NVE ensemble MD. From the distribution of window sizes in Fig. S3 and data in Table T3 (both in the supporting information), it was confirmed again that the better structures were gained from GAFF and GAFF 0.69 force fields. The window size in ZIF-90 from DREID. 0.69 (3.735 Å) is quite larger than GAFF (3.555 Å), GAFF 0.69 (3.525 Å) and experiment (3.5 Å). The smaller width of the window size distribution of modified DREIDING in comparison to GAFF and modified GAFF indicates a smaller flexibility as already found for ZIF-8 in Ref. [15]. In Ref. [15] this prevented the diffusion of methane even with flexible DREIDING but, in ZIF-90 the window size is somewhat larger than in ZIF-8.

From these above results, it is concluded that the modified GAFF can produce not only the adsorption isotherms that fit to the experiment but can also keep the structural quantities like box size in NPT and, more important, window size, well. On the other hand, modified DREIDING just only gives adsorption isotherms in good agreement with the experiment.

3.2. Static properties

The static properties of guest molecules include radial distribution functions (RDF's) and probability density plots evaluated from the results in NVE ensemble MD with modified GAFF. Some RDF's are compared with those from GEMC.

Probability densities of methane in ZIF-90 during 5 ns simulation time in both rigid and flexible models are plotted in Fig. 4. The red dots represent the sites of guest molecules (methane) in snapshots taken every 100 steps from the last 50,000 steps to visualize the probability density to find methane at different sites of the framework. As we can see from Fig. 4, the density clouds of methane molecules are connected with each other in a flexible framework while they are isolated in the rigid framework.

In the rigid model, methane molecules cannot pass through the narrow aperture to enter the next cage. Hence, they only move within the cage. The reason is that the diameter of methane (3.8 Å) is bigger than the window size in ZIF-90 (only 3.5 Å). However, due to the flexibility of the framework, methane molecules can pass the windows in moments in which the window size is temporarily larger than the average window size [35]. Interestingly, our MD simulation showed that in Fig. 4a (rigid model), there is no methane between two cages in all concentration of guest molecules while in Fig. 4b methane molecules can be found in the connecting area between the cages through six-membered rings. In this case methane molecules not only moved inside the cage but also diffused from one cage to other cages.

Fig. 5 shows the RDFs between guest molecules with selected atom types of lattice and guest-guest interaction. The atom types in ZIF-90 were named in Fig. S1 in the supporting information. These RDFs were taken from the GEMC (MC_rigid) at 1 bar, MD with flexible and rigid model at very low loading of 0.5 molecules/cage (1 bar) to compare with each other. In Fig. 5d, while methane in rigid model in MD cannot have the normal distribution due to the blockage of particle exchange between different cages, the random insertions and removals of guest molecules in GEMC, lead to particle exchanges even if we assume the framework in GEMC to be rigid. Fig. 5a–c shows the influence of the flexibility of the framework on the adsorption isotherm. In general, the RDFs from rigid MC show a better agreement with flexible MD than rigid MD.

To decide if the uptake in rigid lattice GEMC and flexible lattice MD at given pressure is equal, it would be necessary to measure the pressure in flexible lattice MD. The pressure calculation *e.g.* using the virial theorem is ambiguous for porous solids for several reasons (as mentioned above) particularly in presence of partial charges and at high pressure. A more appropriate quantity to decide about the equilibrium between different systems in such cases is the chemical potential that must have the same value for each species in all parts of a system that are in equilibrium with each other. The chemical potential μ can be obtained from the Gibbon program and from selected snapshots taken from the trajectory of an MD simulation by Widom's particle insertion method. Using μ instead of the pressure as the independent variable of state, the uptake is plotted in Fig. S4 of the supporting information. In the low concentration (low pressure) area, the results from GEMC and flexible MD are in quite good agreement. Slightly larger deviation appears only at high concentrations (high pressure). These results again support the possibility that an adsorption isotherm can be obtained from rigid lattice GEMC simulation.

3.3. Adsorption sites

In numerous previous papers on MOFs and ZIFs it was found that sometimes the metal ion is the preferential site for adsorption

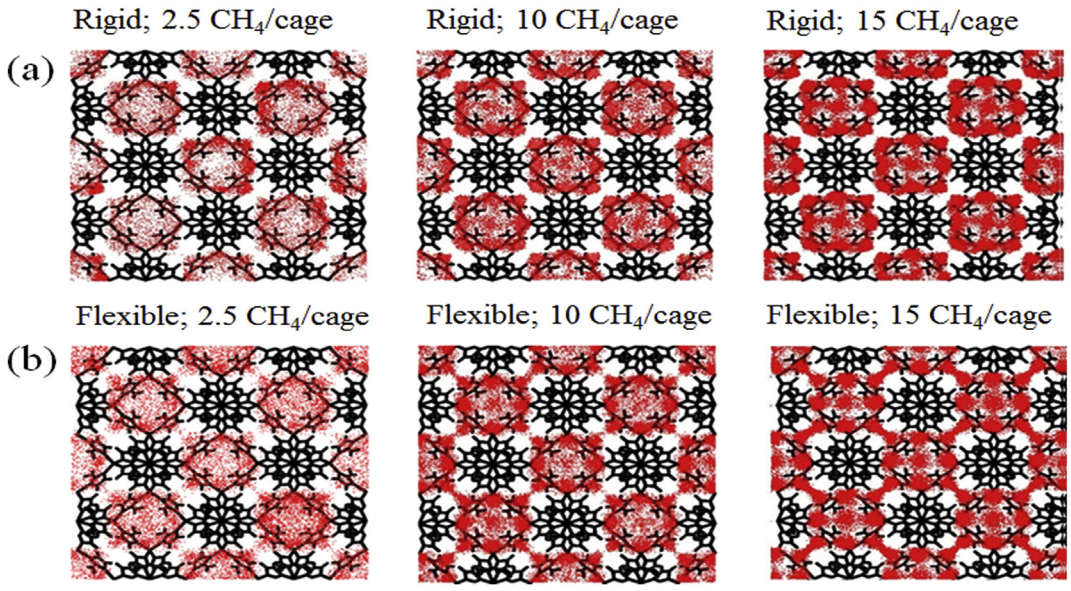

Fig. 4. Probability density of CH_4 in (a) rigid model and (b) flexible model at 2.5, 10 and 15 CH_4 molecules/cage.

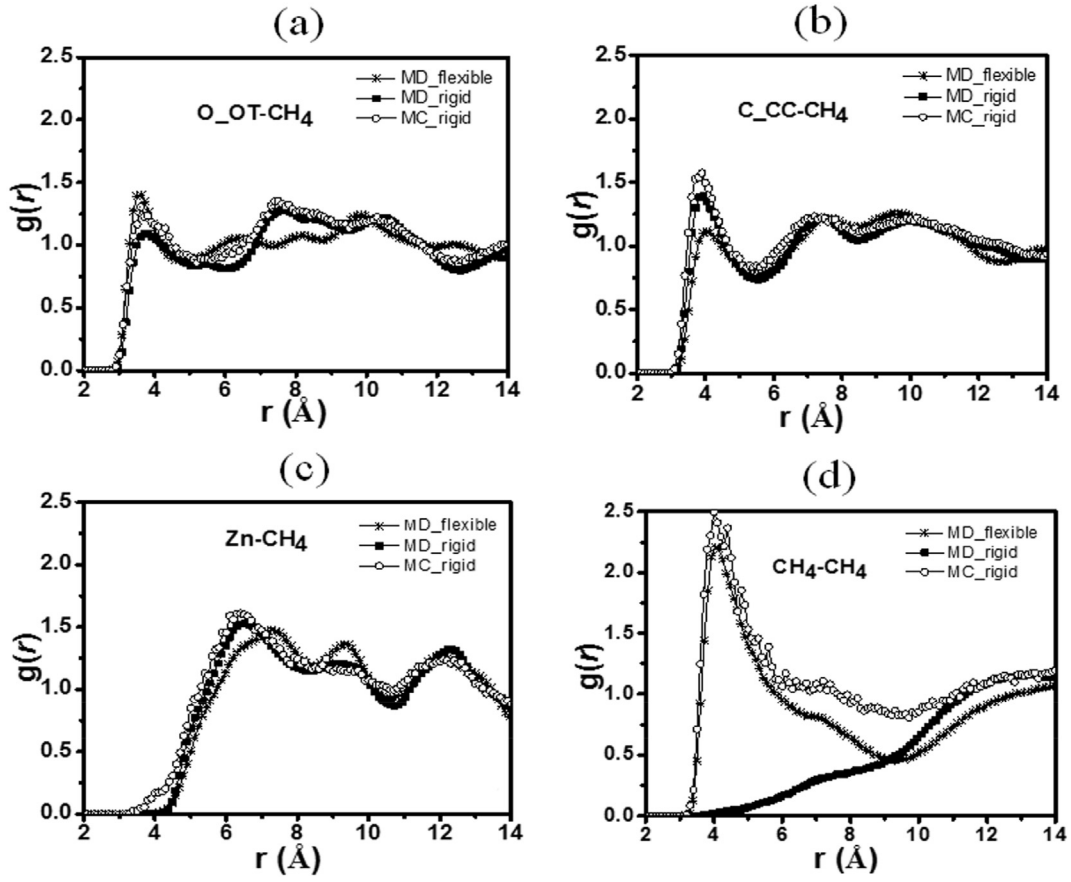

Fig. 5. RDFs of the interaction between methane-methane and methane-ZIF-90 lattice in GEMC, rigid and flexible MD simulations at very low loading (0.5 CH_4 molecules/cage) with modified GAFF at 300 K.

like H_2 in MOF-505 or CO_2 in IRMOFs [36,37]. In other ZIFs the organic linkers interact strongly with the guest molecules and these became the preferential adsorption sites like for alcohol in ZIF-90, H_2 in various ZIFs or CH_4 in ZIF-3, 10 [22,38,39]. For a deeper understanding of the adsorption process, the adsorption site was studied.

The radial distribution functions (RDFs) between methane and selected atoms in the framework are plotted at very low (0.5

molecules/cage) and at very high (15 molecules/cage) loadings in MD simulation with modified GAFF force field. The RDFs between methane and all atom types are given in the supporting information (Fig. S5).

At low loading (0.5 molecules/cage), the first RDF peak for Zn–CH_4 appeared at around 7.5 Å which was very large since the favorite distances between the metal ion (Zn) and the guest molecules (CH_4, CO_2 and N_2) in common ZIFs are around 2–4 Å [23]. Furthermore, the distances measured from CH_4 to O_OT and C_CC were found to be shorter (3.6 and 4 Å) than the distance between CH_4 and Zn. Thus, at low loading, methane molecules are preferentially located at the organic linker or - in other words - the preferential adsorption site is the organic linker. Among them, the 1st peak at O_OT is the closest and highest one. It is not surprising that O_OT is the most favorite site of methane based on the strong van der Waals interaction between O and CH_4. The next peak belongs to C═C in the ring where the distance around CH_4 is about 4 Å. This agrees with other work, in which the adsorption sites of alcohol with ZIF-90 are also C═O of the aldehyde group and C═C in the organic linker [6]. At very high loading, it is clear that the peaks became higher and the distances became closer, especially the favorite distance between Zn–CH_4 was shifted from 7.2 Å to around 6 Å. RDFs of C═O and C═C with CH_4 in different concentrations were also plotted in Fig. S6.

It should be noted that the density plots also visualize the positions of methane in ZIF-90, which is in accordance with the RDF results. Especially at lower loading, the high density area of the point cloud representing the density of methane was near at the organic linker at 2.5 methane molecules/cage. At higher loadings up to the concentration of 15 methane molecules/cage, the adsorption sites extended to the Zn metal ion. This corresponds to the closer peak of the RDF between Zn and methane in Fig. S5.

As mentioned above the pressure at high loadings can be obtained from the Peng-Robinson equation of state applied to the gas phase in box A. At 15 molecules/cage the pressure is around 255 bar. Methane in the gas box of our simulation is still a gas at that pressure and temperature. It is difficult to reach such pressures in experiments but, such experimental investigations have been done already in some cases. *E.g.* in Ref. [40] measurements with ZIF-8 have been carried out at 14,700 bar under loadings up to 41 methanol molecules per unit cell.

The adsorption isotherm from 0 to 255 bar from GEMC simulations with the modified force field GAFF can be seen in Fig. 6. Bulk methane at 300 K has no gas-liquid phase transition. The adsorption isotherm is of Langmuir type and does not show any inflections.

3.4. Dynamical properties

The dynamical properties of guest molecules were examined by calculating their self-diffusion coefficient (D_s). The dynamical behavior of the lattice was investigated by the window size distribution. These results have been obtained in NVE ensemble MD.

Based on the Einstein's relation, D_s can be calculated from the slope of the mean square displacement (MSD) as a function of the observation time. To examine the effect of framework flexibility to the diffusion, MD simulations were conducted on both rigid and flexible framework models. The MSD in the rigid frameworks are shown in Fig. S7. The D_s data are given in Fig. 7 and compared with the previous work of Atci et al. [11] who used a UFF rigid model for MD simulation. The D_s of methane was calculated to be zero in the DREID. 0.69 rigid model (see Fig. S7) that means that no methane diffusion in ZIF-90 could be proven by this model.

In Fig. 7 we can see the big gap of the D_s data between rigid and flexible framework. The methane can diffuse several orders of magnitude faster in the flexible model than in the rigid one. However results for D_s, from the flexible force fields, modified DREIDING, modified GAFF and original GAFF are similar. The larger average window diameter of DREIDING obviously compensates the influence of the lower flexibility for methane in ZIF-90 for this force field that can be seen in Fig. S3 of the supporting information.

In Atci et al. the authors tried to compare their results with experimental permeation measurements. However, their predicted permeances for relative large molecules like methane, nitrogen were much lower than the experimental data. In Ref. [11] this was explained by the underestimation of D_s leading to a small permeance of these molecules. According to [11] the rigid framework was the reason. Therefore, to obtain a more suitable D_s, a flexible model is necessary. From the adsorption isotherm and D_s at 200 °C and 1 bar with modified GAFF, the permeability was calculated by the below formula [12]. The permeance of methane through ZIF-90 obtained in this work is 3.5×10^{-8} (mol m^{-2} s^{-1} Pa^{-1}). This is twice the experimental value of Huang et al. [9] which is 1.57×10^{-8} (mol m^{-2} s^{-1} Pa^{-1}). Nevertheless, our value is nearer to the experiment than the value from rigid model in Atci et al. [11], which is 3×10^{-9} (mol m^{-2} s^{-1} Pa^{-1}). The remaining difference could be explained by imperfect crystals in the real experiment while the crystal is considered ideal in the simulation.

$$P_{ZIF} = \Pi_{ZIF} l = D_s \varphi \frac{c}{f}$$

in which, P is the permeability (mol.m^{-1} s^{-1} Pa^{-1}), Π is the permeance (mol.m^{-2} s^{-1} Pa^{-1}), l (m) is the top layer thickness with

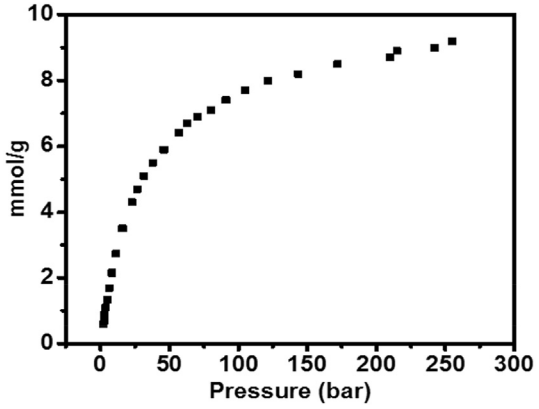

Fig. 6. Adsorption isotherm of CH_4 in ZIF-90 at 300 K for pressures 0–255 bar.

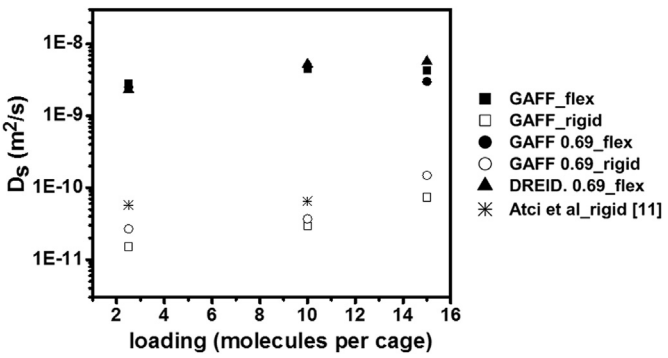

Fig. 7. Comparison of D_s for CH_4 in rigid and flexible ZIF-90 frameworks at 300 K.

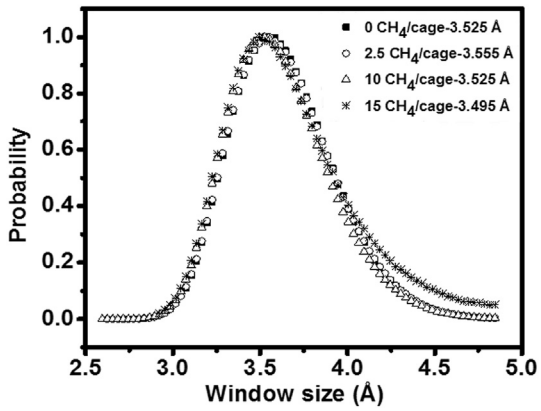

Fig. 8. Distributions of the window size of ZIF-90 for different loadings of CH_4 at 300 K.

l = 20 μm [9],φ is helium void fraction (Widom Insertion method), in ZIF-90, φ = 0.498 [12], c ($mol.m^{-3}$) is equilibrium gas concentration, f (Pa) is the fugacity.

At different loadings of methane in ZIF-90, the average window size of ZIF-90 was nearly unchanged, it increases from 3.525 Å to 3.555 Å at 2.5 CH_4/cage and decrease at very high loading from 3.555 Å to 3.495 Å (Fig. 8).

Throughout the observed range of density and hence pressure up to 255 bar, no discontinuous change of the window size appears. This indicates that no structural change like gate opening can be observed and the experimentally observed adsorption and permeation of "too big methane" molecules is explained by the framework flexibility of ZIF-90.

4. Conclusions

Among the tested force fields, the modified GAFF force field gave the best agreement of the simulated ZIF-90 structure (window size, and box length) and adsorption isotherms with the experiment. With this GAFF force field also the unit cell size could be reproduced in NPT simulations. The behavior of adsorbed guest molecules could be examined on a molecular scale. The flexibility of the framework affects significantly the self-diffusion coefficient D_s of CH_4 in ZIF-90. The D_s obtained from flexible framework is between 1.5 and 2 orders of magnitude higher than D_s obtained for a rigid framework. The reason is that methane molecules can pass through the window in the flexible model. This was visualized by probability density plots and confirmed by the window size distribution.

The window size is nearly independent upon the pressure. Hence, no structural change like gate opening has been observed for the methane/ZIF-90 system up to 255 bar.

The RDFs showed that the adsorption site for methane in ZIF-90 at low loading is mainly the organic linker. At higher loading, also the Zn ions become adsorption sites and also the cage centers and even the windows connecting adjacent cages show a reasonable probability for methane. An adsorption isotherm from 0 to 255 bar could be obtained for which experimental data for the high pressures are still missing.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.micromeso.2016.06.029.

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THE JOURNAL OF PHYSICAL CHEMISTRY C

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Importance of ZIF-90 Lattice Flexibility on Diffusion, Permeation, and Lattice Structure for an adsorbed H_2/CH_4 Gas Mixture: A Re-Examination by Gibbs Ensemble Monte Carlo and Molecular Dynamics Simulations

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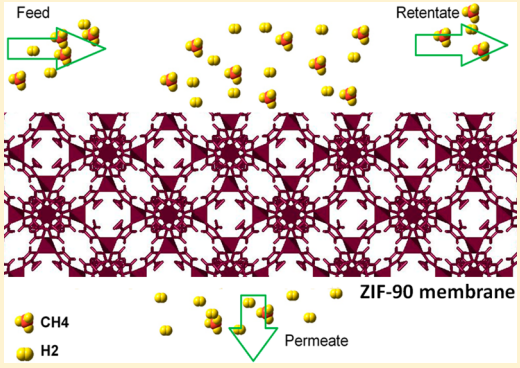
ABSTRACT: Adsorption and diffusion of the gas mixture H_2/CH_4 in the metal−organic framework (MOF) of structure type zeolitic imidazolate framework-90 (ZIF-90) are revisited. While the adsorption can successfully be examined in Gibbs ensemble Monte Carlo (GEMC) simulations using the common approximation of a rigid lattice, the dynamics of methane in ZIF-90 is remarkably influenced by the lattice flexibility. Molecular dynamics (MD) simulations not only show a strong influence of the lattice flexibility on the diffusion of methane but even find a slight structural phase transition of the lattice. This structural change appeared at higher temperatures and was not caused by the content of guest molecules like in most former discoveries of gate opening. For prediction of mixed gas ZIF-90 membrane selectivity, the adsorption and diffusion results show that the high CH_4 adsorption selectivity is overcompensated by the high H_2 mobility. The comparison of our results for the H_2/CH_4 membrane selectivity with experimental findings from mixed gas permeation through supported ZIF-90 membranes shows better agreement than other simulations that use a rigid lattice for MD. Also, the increase of the membrane selectivity by increased temperature could be found.



1. INTRODUCTION

With a narrow window size of about 3.5 Å and exceptional thermal and chemical stability, the metal−organic framework (MOF) zeolitic imidazolate framework (ZIF) of structure type ZIF-90[1] is proposed as a promising candidate for a gas separation material. In the ZIF-90 structure, zinc ions are interconnected by imidazole-2-carboxyaldehyde linker molecules forming a sodalite (SOD) framework structure. Among the gas mixtures to be separated, hydrogen (H_2) is of special interest, e.g., as a future fuel in a PEM fuel cell or for catalytic hydrodesulfurization of natural gas or refined petroleum products. Hence, the process of hydrogen separation from mixtures, e.g., the H_2/CH_4 mixture, is highly interesting. In 2010, Huang et al.[2] used ZIF-90 as a membrane for hydrogen purification with the expectation of a high separation factor due to the different diameters of H_2 (2.9 Å) in comparison with other larger gases like CH_4, CO_2, and N_2 (3.3−3.8 Å). However, the selectivity values from mixed gas permeation experiment are lower than the ideal separation factors predicted from single gas permeation studies. This experimental finding is attributed to the flexibility of the lattice so that guest molecules with kinetic diameters larger than the window size are able to enter the MOF framework, thus passing the membrane.[2−7] In addition to this, heating the ZIF membrane up to 200 or 225 °C could surprisingly increase the effectiveness of the separation on this membrane.[2,4−6] Therefore, a theoretical study of molecular adsorption and diffusion at different temperatures is desirable to obtain deeper understanding of these processes on the atomic scale.

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Recently, in some papers, e.g.,[8,9] diffusion and adsorption in a large number of different ZIF structures have been investigated in order to provide the experimentalists hints on promising candidates for gas separation materials. In Atci et al.,[8] 15 different ZIF materials have been screened, and in Haldoupis et al.,[9] there were even 504 MOF structures. Such overviews are very helpful, but the large number of investigated systems also has its price. Such a huge amount of calculations with flexible lattice MD are hardly possible. In the input file of an MD program package, about 10 000 elastic bonds, angles, and dihedral angles have to be defined explicitly for each flexible lattice, and the computer time needed for MD is increased drastically. Hence, all these papers use only a rigid lattice for MD. This is no big problem for molecules smaller than all the apertures in the lattice. Hence,[8] good agreement with the experiment is obtained for CO_2 (3.3 Å) in ZIF-90 (3.5 Å), but e.g., the permeance for CH_4 (3.8 Å) is underestimated. In ref 9, the selectivity for H_2/CH_4 separation using ZIF-8 was predicted to be 10^7 because the kinetic diameter of methane is larger than the window diameter in rigid ZIF-8 (3.4 Å). In ref 10, MD simulations with flexible lattice led to a H_2/CH_4 selectivity of 13 that was in good agreement with the experimental value of 16.

In many ZIF structures, phenomena connected with strong framework flexibility are observed. Besides window size breathing by lattice vibrations, linker distortions can also cause a modified aperture size, called gate opening. This name is used for a structural change of the lattice that leads to larger windows that connect adjacent cavities without remarkable change of the size of the other parts of the lattice.[11,12] These effects could meanwhile be reproduced in several MD simulations with a flexible lattice.[13−15] The effect of gate opening can be found, of course, only in flexible lattice simulations.

Hence, the question arises whether there is also a gate-opening effect in ZIF-90. In ref 7, no structural change for CH_4 in ZIF-90 was found at pressures up to 260 bar at ambient temperature.

Another important question is the temperature dependence of diffusion and adsorption in combination with the lattice structure. While some MOFs have negative thermal expansion like MOF-5 or HKUST-1,[16] others show a small positive effect of the temperature on the volume of the framework with increasing temperature like ZIFs with SOD topology.[17] Kolokolov et al.[18] found in ^2H NMR experiments for some ZIFs that the temperature influences the reorientation of the organic linker, such as the methyl group in ZIF-8.

Moreover, the Caro group[2] did permeation experiments at various temperatures on hydrogen purification by using a supported ZIF-90 membrane and simulated the influence of temperature and pressure on diffusivity and adsorption of the CH_4/H_2 mixture in ZIF-90. However, the reason for the increase of D_s at higher temperature could be caused not only from the kinetic effect but also from other factors like a change of the structure.

Therefore, in this work, ZIF-90 was studied at various temperatures and guest loadings to investigate the effect of the temperature and of the guest adsorption on the structure of ZIF-90.

In this work, adsorption and diffusion for the 1:1 gas mixture H_2/CH_4 are studied. The results are compared with experimental data and other simulation studies. In addition, the adsorption selectivities and the membrane separation factors are calculated and evaluated. Favorite adsorption sites are determined by the radial distribution functions (RDFs) and the probability densities.

Furthermore, adsorption constants K's and the diffusion coefficients (D_s's) of the guest molecules CH_4 and H_2 inside ZIF-90 at different temperatures have been determined by molecular dynamics (MD) and Gibbs ensemble Monte Carlo (GEMC) simulations.

The size distribution of the window diameter has been checked at different temperatures and loadings in order to find a possible gate-opening effect.

2. SIMULATION DETAILS

The structure of the ZIF-90 framework was taken from the CCDC database.[1] Then, the simulation box was built of 2 × 2 × 2 unit cells for MD simulations and 4 × 4 × 4 for GEMC simulations. Force fields of ZIF-90 and CH_4 were chosen from a previous study[7] while the force field of H_2 was obtained from Grazzi et al.[19] Both guest molecules in this case are considered to be united atoms. While this approximation is well-known for CH_4 (acentric factor of 0.01[20]), arguments for the case of H_2 are given in ref 19.

For the MD simulations, the system was first conducted in NVT (canonical ensemble) to control the temperature for 5 ns, and then the results were analyzed by MD simulations in the NVE (microcanonical ensemble) for 10 ns with a time step of 2 fs. NVE was chosen for the examination of the diffusion in order to exclude artifacts from thermalization. The concentrations of guest molecules of the H_2/CH_4 mixture (ratio 1:1) are 0.5, 2.5, 10, and 15 total molecules/cage. The simulations were also carried out at three different temperatures, 300, 373, and 473 K.

All MD simulations in this work were run by the simulation package DL_POLY 2.20. The Nose−Hoover thermostat was used in the NVT simulations. The self-diffusion coefficient D_s has been evaluated using the Einstein relation.

$$\langle r^2 \rangle = 6D_s t \tag{1}$$

This holds for large time t. $\langle r^2 \rangle$ is the average of the square of the displacement of a particle during the time t (mean square displacement, MSD). In practice, D_s is calculated from the limiting slope of the mean square displacement as a function of time.

Gibbs ensemble Monte Carlo (GEMC) simulations are carried out with the homemade software Gibbon, as in ref 7. This method relies on the simultaneous Monte Carlo simulation of a gas phase and a phase adsorbed in a solid with random exchange of particles between both systems establishing (adsorption) equilibrium. Particle shifts, rotations, and swaps between the boxes are attempted with the relative frequencies 5:5:2.

Also, the partial charges have been treated as described in detail in ref 7. In this method, all the Coulomb potentials of the partial charges of each individual neutral molecule are treated together as a sum, leading to a fast decay of this sum at large distances. Cutoff effects, caused by the slightly different positions of the partial charges within one molecule, are avoided. This method resembles the method for charge groups proposed in ref 21.

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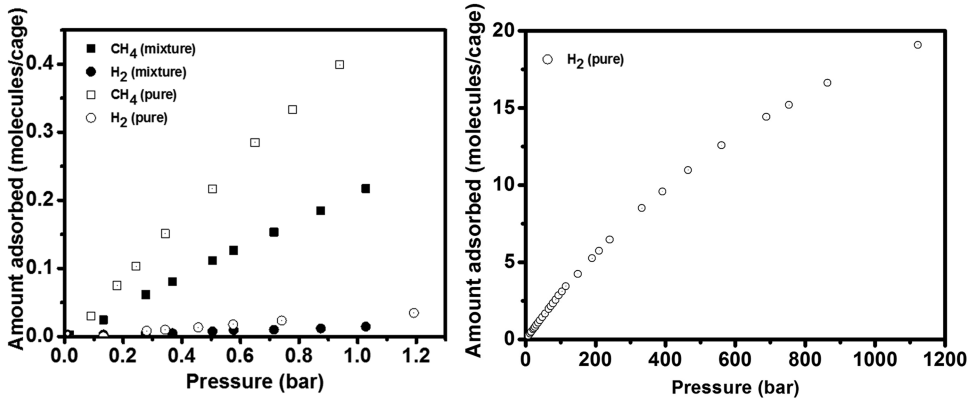

Figure 1. Adsorption isotherms of the single components CH_4 and H_2 as well as of the equimolar H_2/CH_4 mixture in ZIF-90 at 300 K (left-hand side) and the adsorption isotherm of pure H_2 at 300 K up to 1122 bar (right-hand side). Note that the abscissa data give, in the case of the mixture, the total pressure as sum of the partial pressures.

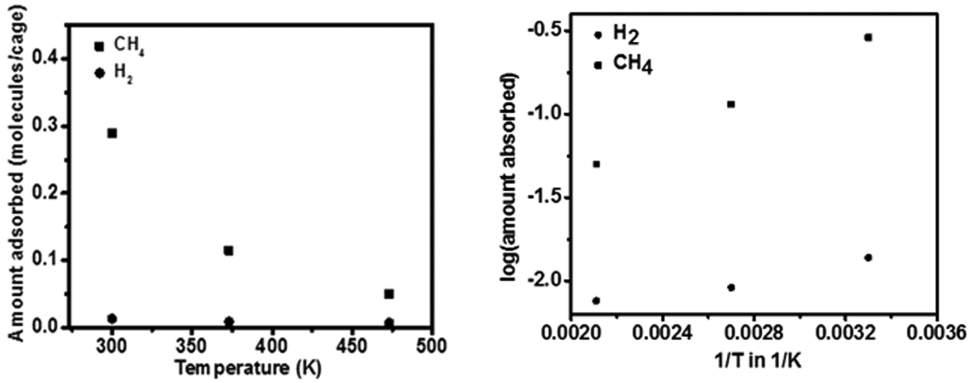

Figure 2. Left: Adsorbed amounts of CH_4 and H_2 as a function of temperature at 1 bar total pressure of the equimolar gas mixture H_2/CH_4. Right: The same as an Arrhenius plot.

3. RESULTS AND DISCUSSION

3.1. Adsorption. Adsorption isotherms of CH_4, H_2, and the H_2/CH_4 mixture at 300 K obtained from GEMC simulations are collected in Figure 1.

The adsorption curves are linear and point to the origin, which means they belong to the linear Henry law region that starts at (0, 0). For comparison, in the case of methane in ZIF-90, it was found that the linear relationship is valid up to about 10 bar.[7] The isotherm for H_2 in Figure 1 (right-hand side) shows that the linear law is valid for hydrogen even up to much higher pressure.

The amount of hydrogen adsorption from the pure gas as well as from the equimolar mixture is much smaller than that of CH_4 as can be seen in Figure 1. The uptake u as a function of the pressure p follows a linear law that resembles Henry's law.

$$u = K \times p \tag{2}$$

The adsorption constant K has been found from the simulations (average slope of the linear curves in Figure 1) to be

CH_4 pure: $K = 0.42$ molec/(cage bar)

CH_4 mix: $K = 0.21$ molec/(cage bar)

H_2 pure: $K = 0.031$ molec/(cage bar)

H_2 mix: $K = 0.015$ molec/(cage bar)

Note that the statistics of the H_2 values is a bit poor because of the small amount of adsorbed particles.

The factor of 2 between the K values of pure substances and those in a mixture agrees well with ideal gas mixture laws because at a given total pressure in an equimolar mixture the partial pressure of each substance is half of the total pressure.

From these adsorption data, the adsorption selectivity of the 1:1 mixture CH_4/H_2 (that means 1:1 in the gas phase) at 300 K is 14.2 independent of the pressure. This high selectivity makes ZIF-90 a promising candidate as adsorbent for, e.g., pressure swing separation of H_2/CH_4 mixtures although the pressure in such processes will be higher than 1 bar, but still in the linear range.

The reason for the higher adsorbed amount of CH_4 in comparison with H_2 is attributed to the stronger attraction between methane and the lattice atoms of ZIF-90.

In addition, the adsorption of the H_2/CH_4 mixture was also evaluated at three different temperatures as shown in Figure 2. As expected, the amounts adsorbed decrease with increasing temperature.

The right-hand side picture in Figure 2 shows an Arrhenius form curve of the uptake as a function of the temperature. The straight lines indicate that not for adsorption but for the desorption an Arrhenius law is valid.

This temperature dependence can be easily understood by applying the lowest term of the fugacity expansion which can be used for the linear part of the adsorption isotherm (like Henry's law).[22] An effective free volume V_{eff} is defined by eq 3.

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$$V_{\text{eff}} = \int d^3\mathbf{r} \exp\{-\beta\Phi_z(\mathbf{r})\} \quad (3)$$

β is $1/k_BT$, where k_B is Boltzmann's constant and T is the temperature. The volume integration has to be carried out over all positions $\mathbf{r}$ of a single guest particle in the ZIF lattice that contains no other guest molecules, and $\Phi_z(\mathbf{r})$ is the potential energy of the single particle at position $\mathbf{r}$.

The number $\langle N\rangle$ of adsorbed particles is related to the effective volume as described by the following equation that has the same shape as an ideal gas equation of state.

$$\langle N\rangle = \beta V_{\text{eff}} p \quad (4)$$

In both formulas 3 and 4, the increase of the temperature leads to smaller effective volume and to smaller $\langle N\rangle$ as well. For a detailed derivation, see ref 22.

Equation 4 is in principle a modification of eq 2; however, the number $\langle N\rangle$ is used instead of the uptake u, and βV_{eff} corresponds to the constant K.

The corresponding CH_4/H_2 adsorption selectivity for the equimolar mixture amounts to 14.2 (0.07) at 300 K, 7.1 (0.14) at 373 K, and 3.6 (0.28) at 473 K (data in parentheses are the H_2/CH_4 selectivities).

Atci et al.[8] found at ambient temperature in GCMC simulations a CH_4/H_2 adsorption selectivity of around 15 which agrees very well with our data. This agreement can be expected because the approximation of a rigid lattice works well for the prediction of adsorption, and we also do the GEMC with rigid lattice. The independence of the adsorption selectivity upon the pressure was also found in ref 8.

3.2. Diffusion. The self-diffusion coefficient D_s of the guest molecules has been calculated at 3 different temperatures corresponding to the experiment and is shown in Figures 3 and 4. Unfortunately, the diffusion calculations for H_2 could not be done in the mixture that is adsorbed from the equimolar gas mixture because the number of adsorbed H_2 molecules is too small to calculate D_s with satisfactory accuracy. However, at low pressure there is minimal interaction between the diffusing molecules, and they should diffuse independently of each other. Hence, we perform the MD simulations as equimolar in the ZIF, and we assume that the D_s of hydrogen obtained in this way at quite low loading can be used also as an approximate value for the lower loadings. Additionally, we check the loading dependence of the D_s at higher pressure where it can be obtained from MD more easily.

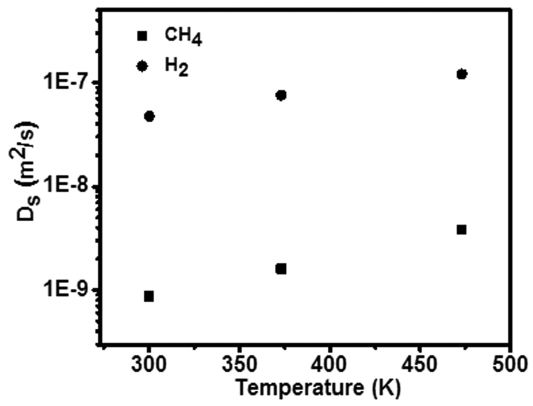

Figure 3. D_s of CH_4 and H_2 in H_2/CH_4 mixture at different temperatures at a very low loading (0.25 CH_4 + 0.25 H_2 molecules/cage) in ZIF-90.

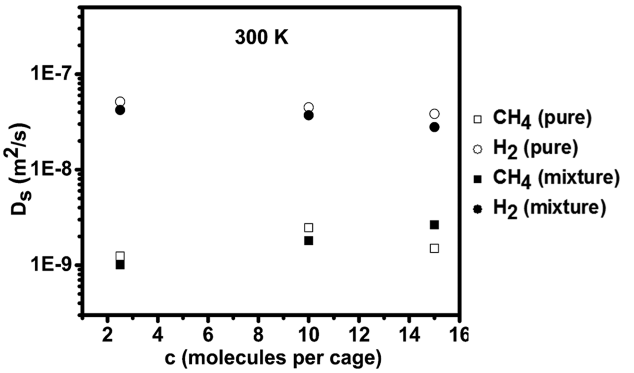

Figure 4. D_s at three different loadings for the pure components CH_4 and H_2 as well as the equimolar adsorbed H_2/CH_4 mixture at 300 K. This is to say, in the case of the mixture, from 8 molecules per cage, 4 CH_4 and 4 H_2.

The temperature dependence in the pressure region that is of interest for comparison with the permeation experiments of ref 2 at 1 bar is shown in Figure 3.

With the increase of temperature, D_s also increases (Figure 3). This is the usual temperature dependence of D_s according to the Arrhenius theory because of the higher thermal energy of the particles at higher temperatures. Furthermore, since the adsorption of methane decreases significantly, a smaller number of methane molecules in the ZIF framework have more space to move, and this also leads to the higher D_s for both kinds, especially for H_2. This phenomenon had been mentioned in Huang et al.[2] when they conducted permeation experiments at these three temperatures at 1 bar.

The self-diffusion coefficient D_s depends upon many factors, e.g., the average thermal speed of the molecules. Because D_s is calculated from an average over all particle movements, it depends upon the average window size as well as upon the smaller and larger window diameters and the probability with which they occur. However, also the shape and size of the cages influence D_s.

In order to estimate how strongly D_s depends upon the loading, 3 test calculations have been carried out and are reported in Figure 4. Even if the loading is increased from 2 molecules per cage up to 15 molecules per cage, the D_s values do not change very much. This supports the idea of an extrapolation to low concentration of H_2 where the interaction between guest molecules is negligible, and thus, D_s does not depend upon the concentration of guest molecules. For a discussion of the loading dependence of D_s at higher pressure in more detail, more data points would be necessary, but this is beyond the scope of the present paper.

For pure CH_4, a GEMC simulation up to a loading of 15 molecules/cage (at about 255 bar) has been reported.[7] The adsorption isotherm is then out of the linear range, but saturation has not yet been reached. For H_2 the pressure for 15 molecules/cage is reached at about 800 bar, and the isotherm can be seen in Figure 1 (right-hand side). It is linear up to about 100 bar. In experiments, such pressures can be reached only in special pressure cells.

Remarkably, the self-diffusion coefficients D_s's for the pure single component adsorbate and for the adsorbed mixture are not very different from each other if the total amount of adsorbed molecules is the same even for loadings up to 15

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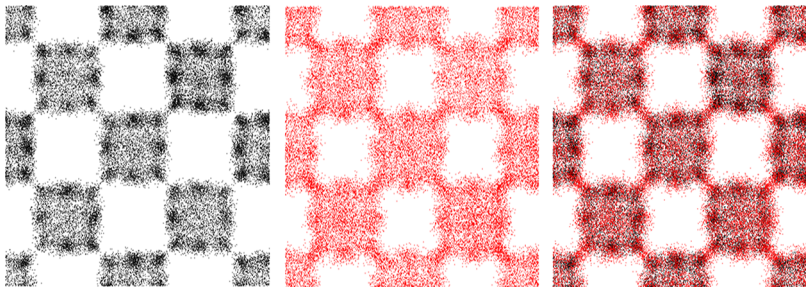

Figure 5. Density distributions of the two kinds of guest molecules at 300 K for 5 CH_4 + 5 H_2 molecules per cage. Red: hydrogen. Black: methane. The picture on the right shows the combination of the two others.

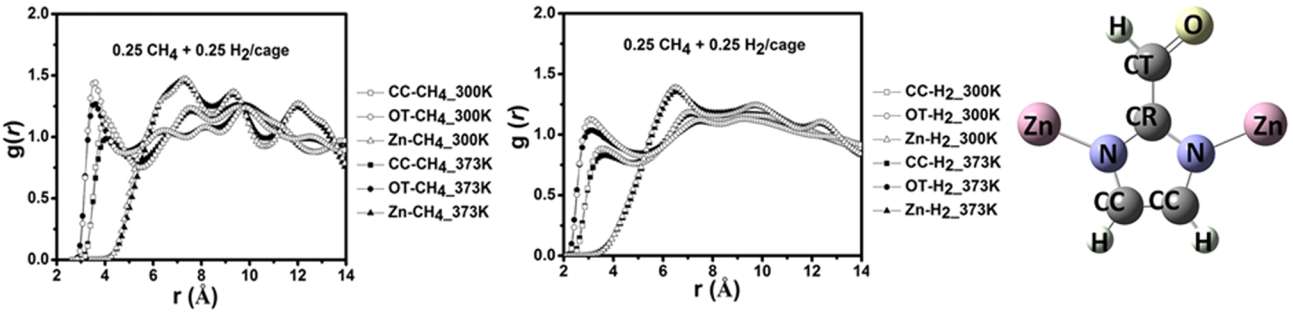

Figure 6. RDFs of the CH_4 and H_2 with selected atoms in ZIF-90 at 300 and 373 K at the low guest molecule concentration of 0.25 CH_4 + 0.25 H_2/cage and organic linker.

molecules per cage. For example, the D_s of H_2 is only slightly smaller if half of the H_2 molecules are replaced by the heavier CH_4 molecules. At high loading, the D_s of CH_4 is somewhat larger in the mixture when half of the CH_4 molecules have been replaced by the lighter H_2. If this is true even at higher loadings, then this finding strongly supports the assumption that the D_s in the low pressure region (1 bar as in ref 2) does not depend on the concentration ratio of the mixture. Thus, the results of our adsorption and diffusion studies, which we need for the calculation of permeation selectivities, can be extended to nonequimolar feed mixtures.

Probability densities of particle locations for the adsorbed H_2/CH_4 mixture are plotted in Figure 5. The red dots refer to the sites of H_2, and the green dots represent the sites of CH_4 in snapshots taken every 100 steps from the last 50 000 steps in MD simulations to describe the position probability of methane and hydrogen during simulation time.

It can be seen that, at this quite high density, both kinds of molecules are distributed over the whole cavity. The overlay shows that some H_2 molecules reside closer to the cavity walls than any CH_4 molecule. However, this is probably only due to the smaller diameter of H_2.

For low adsorbate densities, the statistics is too poor for such a density plot. Therefore, the structure of the adsorbed mixture at low density has been investigated by the radial distribution function (RDF). The results can be seen in Figure 6.

At low adsorbate density, favorite adsorption sites of both CH_4 and H_2 are the oxygen atoms of the aldehyde group of the linker in the ZIF-90 lattice. Other sites of high probability are CC, which means the organic linker is in agreement with many other ZIFs and with the single gas CH_4 in ZIF-90 in the previous work.[13−15,23−26]

3.3. Comparison of our MD Calculations with Permeation Experiments. For a comparison of the results with the experiment, the permeability is calculated from the adsorption and diffusion data by the following equation. The results are shown in Figure 8.

$$P_{ZIF} = \prod_{ZIF} l = D_s \phi (c/f) \tag{5}$$

In this equation, the following abbreviations apply: P is the permeability (mol m^{-1} s^{-1} Pa^{-1}), Π is the permeance (mol m^{-2} s^{-1} Pa^{-1}), l (m) is the top layer thickness with l = 20 μm^2, ϕ is the helium void fraction (Widom insertion method; in ZIF-90, ϕ = 0.498[27]), c (mol m^{-3}) is the equilibrium gas concentration, and f (Pa) is the fugacity.

In Figure 7, the simulation results of this work are shown for the permeance, with a rather good agreement with the experiment.[2] While the permeance of H_2 agrees quite well with the experiment, the permeance of CH_4 is slightly overestimated. Atci's work,[8] which uses a rigid framework

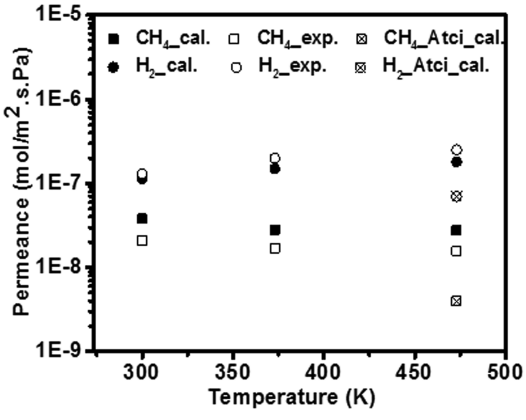

Figure 7. Comparison of the calculated membrane permeances for the equimolar H_2/CH_4 mixture in comparison with the permeation experiment[2] and Atci's work.[8]

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model for the calculation, yields lower values of the permeance by about half an order of magnitude due to the underestimated D_s.

In addition, from adsorption and diffusion selectivities, the separation factors are also evaluated through the following equation, and then, they can be compared with the separation factor from the permeation experiment on a ZIF-90 membrane at the three temperatures (see Table 1).

$$\alpha_{\text{membrane},H_2/CH_4} = \alpha_{\text{diffusion},H_2/CH_4} \times \alpha_{\text{adsorption},H_2/CH_4} \quad (6)$$

at 300 K: $\alpha_{\text{membrane},H_2/CH_4} = 55 \times 0.07 = 3.9$

at 373 K: $\alpha_{\text{membrane},H_2/CH_4} = 46.5 \times 0.14 = 6.5$

at 437 K: $\alpha_{\text{membrane},H_2/CH_4} = 32.5 \times 0.28 = 9.1$

Table 1. Comparison of the Membrane Selectivity of the H_2/CH_4 Mixture of Our Calculation and the Membrane Permeation Experiment of Huang et al.[2]

	separation factor H_2/CH_4	
temp	expt	calc
300 K	7	3.9
373 K	11	6.5
473 K	15.2	9.1

Table 1 shows a comparison of the membrane selectivity of the H_2/CH_4 mixture of our calculation and the membrane permeation experiment of Huang et al.[2] The results are in fair agreement, although the calculated values are smaller. This can be explained by the assumption of a perfect crystal framework as mentioned in a previous work which leads to a lower separation factor than the experimental one.[2]

3.4. Thermal Effects on the Flexible Lattice: Temperature Induced Structural Change. *3.4.1. Change of the Window Size for the Empty Lattice as a Function of the Temperature.* The change of the window size in the empty framework with increasing temperature was analyzed in order to examine the effect of the temperature upon the structure.

The window size is defined by the diameter of the largest sphere that fits into the window. The procedure has been described in detail in ref 23.

The probability distributions of the window size at different temperatures for the lattice without guest molecules are shown in Figure 8.

The results show that, without any guest loading, the size of the ZIF-90s window is increased from 3.56 Å (at 300 K) to 3.71 Å (at 473 K) while the X-ray structure obtained at 300 K yields 3.5 Å. The increase of the window aperture in ZIF-90 is evident. The same phenomenon was found for ZIF-8 by Kolokolov et al.[18] who found that the effective window size in ZIF-8 could be increased up to 4.7 Å following an increase of the temperature (up to 550 K) so that even benzene molecules could pass through the aperture of ZIF-8.

In order to check if this increase of the window size appears together with an extension of the whole lattice, an additional MD simulation was conducted in the NPT ensemble to study the change of the box length at different temperatures. In contrast to NVE MD simulations, the box size is variable in NPT.

Figure 9 shows that, in contrast to the window size, the total size of the simulation box and hence also the lattice does not change significantly with the increase of the temperature in the NPT simulation. In detail that means that the box length has a positive expansion but with a very small percentage (around 0.03%). This is also in agreement with the types of ZIFs which have SOD topology.[17]

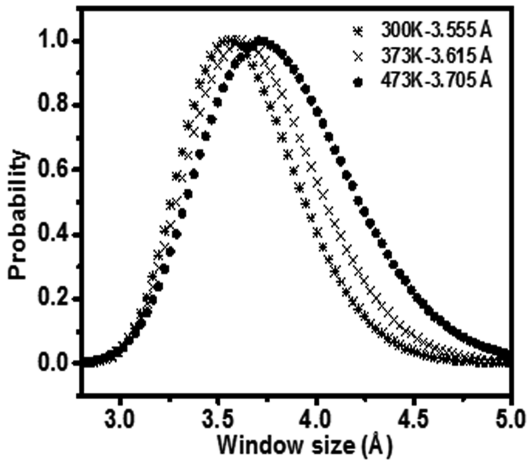

Figure 8. Probability distributions of the window size.

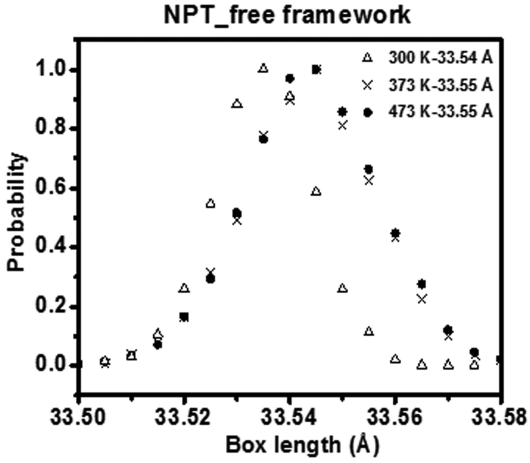

Figure 9. Probability distribution of box length.

3.4.2. Influence of Guest Molecule Loadings. In addition to the pure CH_4 sorption[7] where no structural change appeared in ZIF-90 up to a pressure of 260 bar at ambient temperature, the effect of a CH_4/H_2 mixture on the ZIF-90 structure was also studied.

To explore the influence of the amount of guest loading on the framework, CH_4/H_2 (ratio 1:1) mixtures were assumed to be adsorbed into ZIF-90 at different concentrations: 0.5, 2.5, 10, 15, 30 total molecules/cage. The resulting window size as a function of loading is shown for two temperatures in Figure 10.

Figure 10 shows that the increase of loading of guest molecules did not significantly affect the structure of the framework. Specifically, the window sizes of ZIF-90 at 300 K with and without guest molecules inside are nearly unchanged, around 3.5 Å, and agree with its value in the XRD structure. In contrast with this, it becomes around 3.7 Å by a temperature change to 473 K which is 0.2 Å larger than the XRD experiment reported at 300 K. Again, the results fit well together with the previous study showing that there is no gate-opening effect for loadings of CH_4 inside ZIF-90 at 300 K even up to 15 CH_4 per cage.[7]

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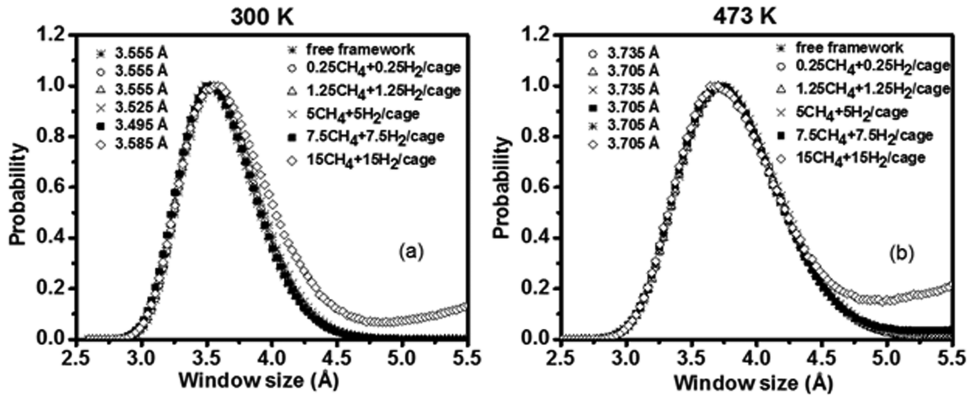

Figure 10. Probability distribution of the window size in two different temperatures: (a) 300 K and (b) 473 K.

4. CONCLUSIONS

MD simulations with a flexible lattice for the diffusion effects and GEMC simulations with a rigid lattice for the adsorption effects predict promising membrane permeation data for the metal−organic framework (MOF) of structure type ZIF-90 for the separation of methane (CH_4) and hydrogen (H_2). H_2 is less adsorbed than CH_4. This is in agreement with results from other papers. The reason is the stronger attraction between CH_4 and the lattice atoms of ZIF-90. Therefore, the reasonable adsorption selectivity CH_4/H_2 of about 14.2 at room temperature could be used in adsorptive separation processes.

For support of this idea, the adsorption isotherm of H_2 has been shown to be linear up to about 100 bar while that of CH_4 was found to be linear up to about 10 bar.[7] Hence, the findings of this paper can be extended to pressures of 6−10 bar that are typical for pressure swing separations.

For gas permeation through a membrane, the adsorption selectivity in favor of CH_4 is overcompensated by the high H_2 diffusivity. The self-diffusion coefficient of H_2 is larger than that of CH_4, and both increase with increasing temperature. The membrane H_2/CH_4 selectivity is predicted to increase from 3.9 to 9.1 by increasing the temperature from 300 to 473 K. Experimental studies of membrane permeation of an equimolar H_2/CH_4 mixed feed through a supported ZIF-90 membrane are in fair agreement with the calculations.

Structural investigations show that favorite adsorption sites of both CH_4 and H_2 are the oxygen atoms of the aldehyde group of the linker in the ZIF-90 lattice, and other sites of high probability are CC (for definition of CC see Figure 6) or the organic linker.

The mixture shows ideal gas behavior up to pressures of 1 bar with respect to adsorption and diffusion. Therefore, these results and the selectivities should be valid for nonequimolar mixtures as well.

A structural change of the lattice was found for higher temperatures that does not depend upon the loading with guest molecules. This is analogous to an experimental finding for ZIF-8 but has, to our knowledge, not yet been observed for ZIF-90 and not been calculated in classical MD simulations of ZIFs. Hence, the importance of the lattice flexibility could be shown once more in the light of the huge effort that is necessary for their realization and in spite of the impossibility to screen so many ZIFs in one paper in this way.

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Notes

The authors declare no competing financial interest.

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