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มหาวิทยาลัยรามคำแหง

รายงานวิจัยฉบับสมบูรณ์

การกำจัดไนโตรเจนออกไซด์จากแก๊สผสมโดยใช้วัสดุที่มีรูพรุน
การจำลองทางคอมพิวเตอร์

โดย ผู้ช่วยศาสตราจารย์ ดร. ตติยา โชคบุญเปี่ยม

2 พฤษภาคม 2563

สัญญาเลขที่ MRG6180001

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ภาควิชาเคมี คณะวิทยาศาสตร์ มหาวิทยาลัยรามคำแหง

สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัย

บทคัดย่อ

รหัสโครงการ: MRG6180001
ชื่อโครงการ: การกำจัดไนโตรเจนออกไซด์จากแก๊สผสมโดยใช้วัสดุที่มีรูพรุน – การจำลองทางคอมพิวเตอร์

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ระยะเวลาโครงการ: 2 ปี

สารประกอบไนโตรเจนออกไซด์ (NO_x) ได้แก่ ไนโตรเจนไดออกไซด์ (NO_2) ไนโตรเจนมอนอกไซด์ (NO) และไดไนโตรเจนเตตราออกไซด์ (N_2O_4) เป็นสารมลพิษทางอากาศที่สำคัญ ที่ก่อให้เกิดมลภาวะต่อสิ่งแวดล้อม และอันตรายต่อสุขภาพของมนุษย์และสัตว์ การกำจัดสารมลพิษเหล่านี้ออกจากก๊าซผสมในอากาศโดยกระบวนการทางเทคนิคทั่วไป เช่น การควบแน่น อาจจะไม่เพียงพอต่อการตอบสนองการปลดปล่อยสารมลพิษอย่างไม่จำกัด ดังนั้นโครงการวิจัยนี้ มุ่งเน้นที่จะตรวจสอบความน่าจะเป็นการใช้งานวัสดุที่มีรูพรุน (โดยเฉพาะอย่างยิ่ง วัสดุโลหะอินทรีย์ชนิดเลียนแบบซีโอไลต์ (Zeolitic Imidazolate Frameworks: ZIFs) และวัสดุโครงข่ายโลหะอินทรีย์ (Metal Organic Frameworks: (MOFs) เพื่อกำจัด NO_x โดยการคัดแยกด้วยกระบวนการดูดซับ หรือเมมเบรน ออกจากก๊าซชนิดอื่นๆ การตรวจสอบว่าวัสดุชนิดใดมีประสิทธิภาพดังกล่าวภายใต้วัตถุประสงค์ ราคาถูก และไม่มีอันตรายต่อสุขภาพ วิธีที่น่าจะเหมาะสมคือ การจำลองทางคอมพิวเตอร์โดยศึกษาปริมาณการดูดซับ และการแพร่ของ NO_x ในวัสดุชนิดต่างๆ เนื่องจากวิธีดับกล่าวไม่มีความเสี่ยงในการทดลองกับสารที่เป็นพิษ ดังนั้นการจำลองทางคอมพิวเตอร์สามารถช่วยหลีกเลี่ยงการทดลองที่ไม่จำเป็น

คำหลัก: การดูดซับ, การแยก, วัสดุโลหะอินทรีย์ชนิดเลียนแบบซีโอไลต์, การคำนวณทางคอมพิวเตอร์

Abstract

Project Code: MRG6180001

Project Title: Elimination of nitrogen oxides from gas mixtures by using of porous materials - computer simulation studies

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Project Period: 2 year

Nitrogen oxides (NO_x) compound including nitrogen dioxide (NO_2), nitrogen monoxide (NO), and dinitrogen tetroxide (N_2O_4) belong to the most prominent air pollutants that cause environment pollution and health risk for human and animals. Their removal of waste gases from mixtures in air by common technical processes like condensation may not be sufficient to fulfill emission limit values. Therefore, this project intends to check a possible use of porous materials (particularly Zeolitic Immidazolate Frameworks (ZIFs) and other Metal Organic Frameworks (MOFs)) to remove NO_x from other gases by adsorption or membrane separation. A promising way to scan several materials for this purpose cheaply and without health risk seems to be computer simulation of adsorption and diffusion of NO_x in such materials. Particularly because of restrictions that apply to experiments with poisoned substances computer simulation can help to avoid unnecessary experiments.

Keywords: Nitrogen oxides, Separation, Porous materials, Computational simulations

1. Introduction to the research problem and its significance

Nitrogen oxides including nitrogen dioxide NO_2, nitrogen monoxide NO, and N_2O_4 belong to the most prominent air pollutants that cause environment pollution and health risk for human and animals. It is created in nature e.g. by bacterial respiration, volcanoes, and lightning. More important is its emission from industrial processes and from internal combustion engines burning fossil fuels [1]. The percentage of nitrogen oxides in the air is carefully watched by international organizations and it forms one important reason for blocking city centers against cars to protect air quality. Indoors, exposure arises from cigarette smoke [2], and butane and kerosene heaters and stoves. Under ambient conditions nitrogen monoxide will be quickly converted into nitrogen dioxide if free oxygen is available as it is the case in air. But, at temperatures above 473 K pure NO_2 dissociates into O_2 and NO. In air under the influence of sunlight NO_2 can dissociate in NO and one highly reactive O that together with O_2 of the air forms the toxic O_3 (ozone). Nitrogen dioxide is toxic. Direct exposure of NO_2 to the skin or to the eyes can cause irritations and burns. Chronic exposure can lead to lung damages and may have even effects on the heart. Nitrogen dioxide is paramagnetic but, the magnetic moment is small and it can therefore be neglected. The NO_2 molecule has a permanent but small dipole moment that is about 10 times smaller than that of a water molecule. In gaseous state NO_2 is in equilibrium with its dimer dinitrogen tetroxide N_2O_4 which is also toxic. At 1 bar the concentration of N_2O_4 in this mixture is about 10 % at 373 K, about 60 % at 323 K and 80 % at 283 K. Below 273 K the mixture contains almost only N_2O_4. The boiling temperature of N_2O_4 is 294.85 K and the melting point is at 261.9 K. At temperatures between the melting temperature and the boiling temperature N2O4 is a liquid. Above 273 K it is of brown color because it contains some NO_2. Higher temperatures and lower pressures shift the equilibrium towards nitrogen dioxide. Dinitrogen tetroxide is also a component of smog containing nitrogen dioxide. In spite of the low boiling point removal of waste gases from mixtures by condensation may not be sufficient to fulfill emission limit values and hence, fundamental research that could lead to complementary methods seems to be desirable.

Porous materials play an increasing role in research and industry. Prominent examples are zeolites, carbon nanotubes, and Metal Organic Frameworks. Zeolites are extensively used in many industrial purposes for decades already as catalysts, molecular sieves, in petrochemical industry, as solar thermal collectors, for heating and cooling and even applications in everyday human life, like in washing agents. Zeolites, adsorbing radioactive substances, have also been used in the cleanup of the 1979 Three Mile Island Nuclear Disaster in the United States and in the nuclear disaster at Fukushima. Carbon nanotubes (CNTs) are used e.g. in electronics (new transistors, improved accumulators) or, because of their low weight combined with very high mechanical stability in the construction of car bodies, airplane wings or wind wheels etc. Several new classes of porous materials have been developed recently. Particularly, during the last decade Metal Organic Frameworks (MOFs, see e.g. ref. [3, 4]) 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 [4]. 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 thus giving the possibility of tailoring the MOFs to specific applications. But, for technical applications also a high stability against thermal and chemical conditions of use and against pressure changes are required. With respect to the stability a subgroup of the MOFs, the Zeolitic Imidazolate Frameworks (ZIFs) are very promising. Their structures are similar to stable zeolitic structures. Many ZIFs have extraordinary high thermal and chemical stability [5] what makes them interesting materials for potential industrial purposes.

Besides experiments, computer simulations are important tools for the exploration of new materials and their applications. 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. Simulations can give hints to find promising experiments, thus avoiding less promising ones, and they can help to improve understanding of experimental results. Surprisingly, there are only few simulation studies about mixtures containing nitrogen oxides and the question how to remove them from gas mixtures.

The possible investigations in this proposal require some pioneering work e.g.

a) Three component mixtures require a quite large number of simulated molecules or very long simulation runs in order to have a satisfactory statistics particularly for the sort with lowest concentration in the mixture. Therefore, simulations of ternary mixtures are quite rare in the literature.

b) The equilibrium ratio between the monomer NO_2 and its dimer N_2O_4 in a mixture depends upon pressure and temperature and cannot be chosen arbitrarily.

c) No results about the equilibrium between this monomer and its dimer within cages of the porous solids examined here have been published up to now.

2. Objectives

Studying the adsorption properties of gas mixtures contain nitrogen oxides into porous materials by Monte Carlo and Molecular Dynamics (MD) simulations studies. Explaining more detailed fundamental insight into migration mechanisms, structure properties like adsorption sites within the porous crystal and the structural arrangement for such mixtures.

3. Methodology

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

3.2 Building structure 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 N_2, O_2, NO_2, N_2O_4 molecules and mixtures NO_2/N_2O_4, $N_2/O_2/NO_2$ and $N_2/O_2/$ N_2O_4.

3.4 Preparing the input files for different loadings of single guest molecule (N_2, O_2, NO_2, and N_2O_4) in ZIFs with various concentrations: 8, 40, 80, 120, 160, 200, 240 molecules 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:

3.4.1 Plot the graph for various Radial Distribution Functions (RDFs) and find the adsorption sites

3.4.2 Analyze the window size for the six-member ring.

3.4.3 Calculate the self-diffusion coefficient (D_s) at all concentrations.

3.4.4 The simulation will be conducted on both rigid and flexible frameworks in NPT, NVT and NVE ensemble.

3.5 Examining gas mixtures such as NO_2/N_2O_4 (ratio;1:1), $N_2/O_2/NO_2$ (ratio;1:1:1), $N_2/O_2/$ N_2O_4 (ratio 1:1:1), comparison with single gas results and calculation of the separation factor and also membrane selectivities.

3.6 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 N_2, O_2, NO_2, N_2O_4 and their mixtures (2 and 3 components)								
Preparing input file for simulations		*						
Running simulations with different concentration of guest molecules (8-240)								
Single gas : N_2, O_2, NO_2, N_2O_4		*						
Mixture gas: NO_2/N_2O_4, $N_2/O_2/NO_2$, $N_2/O_2/$ N_2O_4			*					
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 2 nd system MOFs with N_2, O_2, NO_2, N_2O_4 and their mixtures (2 and 3 component)								
Preparing input file for simulations					*			
Running simulations with different concentration of guest molecules (8-240)								
Single gas : N_2, O_2, NO_2, N_2O_4					*			
Mixture gas: NO_2/N_2O_4, $N_2/O_2/NO_2$, $N_2/O_2/$ N_2O_4						*		
Analyzing results and comparison with ZIFs							*	
4. Writing publications				*				*

5. Expected outputs in ISI

Title: Molecular Simulations of nitrogen oxides from gas mixtures by using of porous materials

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			
- book	5,000	5,000	10,000
- office materials, paper, CD, and thump drive	20,000	20,000	40,000
- upgrade computer	25,000	25,000	50,000
3. Operational costs			
- activity at Thailand research fund	5,000	5,000	10,000
- conferences in Thailand	24,000	24,000	48,000
(transportations and accommodations)			
- copy and print documents	10,000	10,000	20,000
- report	5,000	5,000	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. Separation of nitrogen dioxide from the gas mixture with nitrogen by use of ZIF materials; Computer simulation studies

(Accepted by Computational Materials Science, 13 May 2019.)

The project included the study of the adsorption properties of gas mixtures containing nitrogen oxides into porous materials by Monte Carlo studies with the objective to obtain knowledge that can be used for the removal of nitrogen oxides from gas mixtures by use of porous materials. Adsorption selectivities are to be calculated. Furthermore, Molecular Dynamics (MD) computer simulation studies will yield diffusion coefficients and diffusion selectivities. From adsorption selectivities and diffusion selectivities membrane selectivities can be forcasted. All simulations of mixture NO_2/N_2 were done at 373 K because N_2O_4 will exist only in small percentage. NO_2 can be a product of combustion machines that work at even higher temperatures than 373 K and the emitted exhaust gas can have this temperature. At 373 K the N_2O_4 molecules have a short lifetime. If an N_2O_4 will be formed by dimerization within the cavities of porous materials, then it will influence only short time the adsorption/diffusion patterns before it disappears, even if the probability of formation can be somewhat increased by restricted space and higher pressure.

1.1 Adsorption isotherms and adsorption selectivity

Adsorption isotherms and adsorption selectivity were investigated by Monte Carlo simulations.

Adsorption of pure N_2, NO_2 and O_2 in Zeolitic Imidazolate Frameworks (ZIFs)

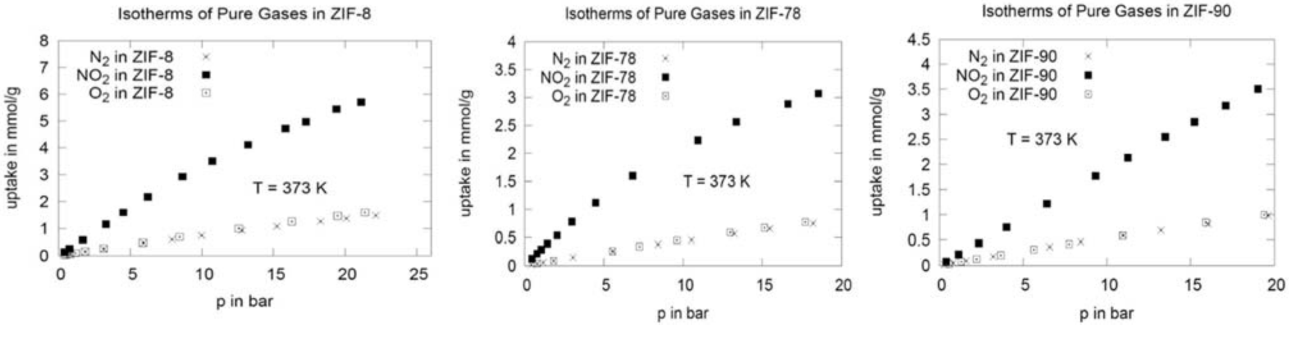


Fig. 1 Adsorption isotherms of pure N_2 and NO_2 as well as O_2 in ZIF-8, ZIF-78 and ZIF-90 at 373 K.

Oxygen was included in order to evaluate the separation of NO_2 from air. It is found that the adsorption isotherm of O_2 is almost identical with that of N_2. This means that the adsorption performance of NO_2 from N_2 will be identical to that of NO_2 from air. A similar observation was made for ZIF-78 at various temperatures in [1]. In [1] it was also shown that in the presence of N_2 and O_2 CO_2 adsorption is comparable.

Adsorption isotherm and adsorption selectivity of the mixture NO_2/N_2

Figure 2 shows the adsorption isotherms and adsorption selectivity of for the mixture NO_2/N_2 in ZIF-8, ZIF-90 and ZIF-78 at 373 K. The adsorption selectivity was calculated by this equation. The definition of the adsorption selectivity $\alpha_{ij}^{\text{adsorption}}$ for adsorption of two species **i** and **j** from a mixture.

$$S_{ij} = Def\,\frac{N_{ads,i} / N_{ads,j}}{N_{gas,i} / N_{gas,j}}$$

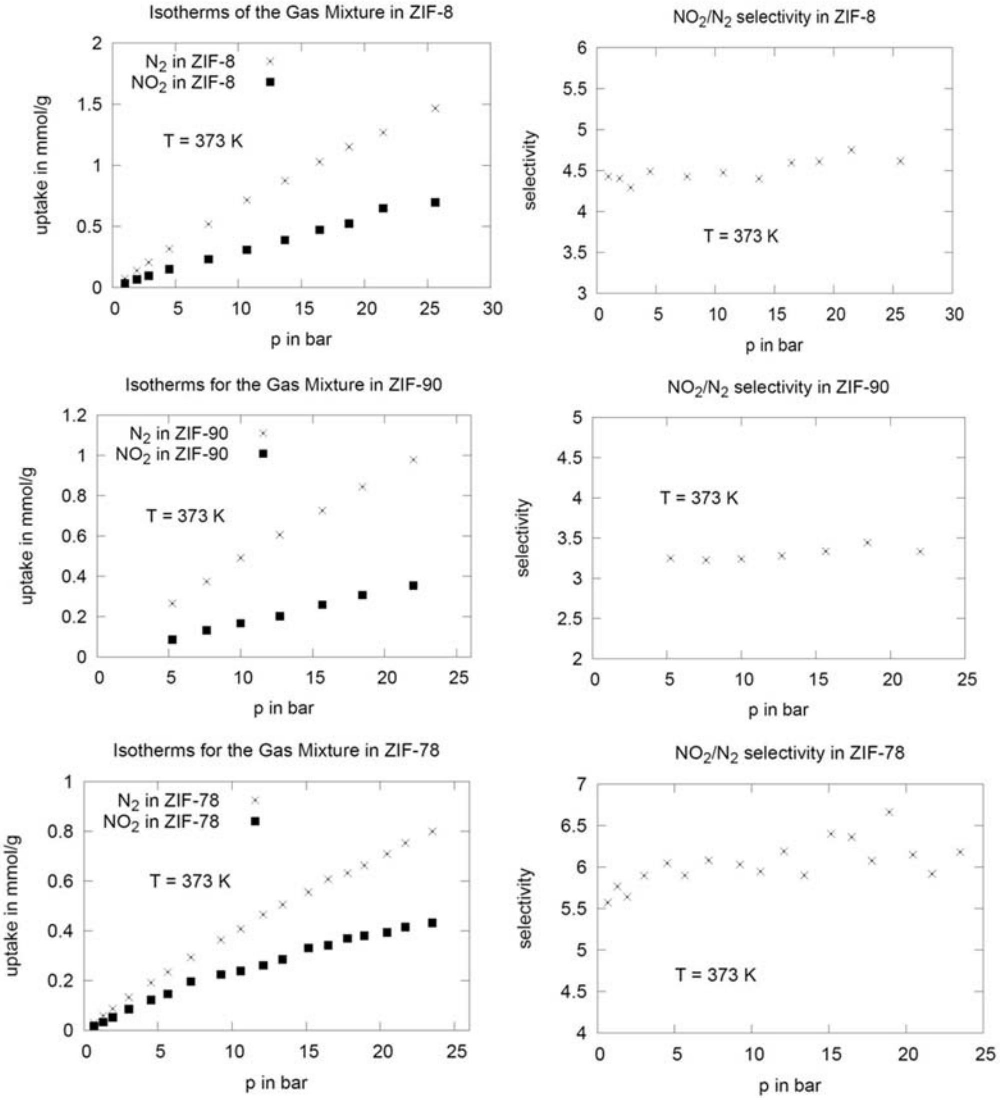


Fig. 2 Adsorption isotherm and adsorption selectivity for the mixture NO_2/N_2 in ZIFs at 373 K.

ZIF-8 may look contra-intuitive that more N_2 than NO_2 molecules are adsorbed, but, the ratio in the gas is 10:1 and if the selectivity would be equal to 1, then the amount of N_2 within the ZIF should be ten times that of NO_2. The adsorption selectivity of ZIF-8 for NO_2/N_2 seems to increase slightly with increasing pressure, but the increase, if any, is within the range of the fluctuations.

ZIF-90, the investigations have not been extended to lower pressures because at 5 bar there are, on average, only about 3 molecules of NO_2 in the simulation box that contains the ZIF, and because of fluctuations quite often the ZIF does not contain any NO_2. The selectivity in this mixture in ZIF-90 like in ZIF-8, a small increase of the adsorption selectivity with increasing pressure within the range of fluctuations, cannot be excluded, also for ZIF-90.

ZIF-78 at 373 K, the content of NO_2 in the connected gas phase was again 10 per cent of that of N_2. As already observed in [1] for the adsorption of CO_2 also for NO_2 the fluctuations for adsorption in ZIF-78 are quite big. This was the main reason to extend the GEMC simulations for ZIF-78 to a larger simulation box and more particles in comparison to the other ZIFs in order to improve the statistics. These fluctuations lead to the scattering of the data for the adsorption selectivity that can be seen in figure 2.

1.2 Self–diffusion coefficients of the mixture NO_2/N_2

The self-diffusion coefficients D_s of NO_2 and N_2 in the mixture at 373 K for the three materials can be seen in table 1 by using Molecular Dynamics (MD) simulations.

Table 1 The self-diffusion coefficients D_s of the N_2/NO_2 mixture in ZIF materials at 373 K.

ZIFs materials	**D_s** of N_2	**D_s** of NO_2
ZIF8	$6.33x10^{-10}$	$7.30\ x10^{-10}$
ZIF78	$3.19\ x10^{-10}$	$1.80\ x10^{-10}$
ZIF90	$1.53\ x10^{-9}$	$1.94\ x10^{-9}$

Table 1 shows a comparison of the self-diffusion coefficients of N_2 and NO_2 in the adsorbed N_2/NO_2 mixture in the three ZIF materials at 10 bar and 373 K. The shifts of one N atom in N_2 and of the N atom in NO_2 have been used for these calculations because the small size of the two molecules and the much larger shifts allow this simplification. It can be seen that the self-diffusion of both components in ZIF-78 is considerably smaller than in ZIF-8 and ZIF-90. This can be important for the flow through a membrane for separation purposes.

Table 2 shows adsorption selectivity, diffusion selectivity and membrane selectivity of the mixture N_2/NO_2 in ZIFs. The diffusion and membrane selectivity were calculated by

$$\alpha_{ij}^{\text{diffusion}} = \mathbf{D}_j^{\text{diffusion}} / \mathbf{D}_i^{\text{diffusion}}$$
$$\alpha_{ij}^{\text{membrane}} = \alpha_{ij}^{\text{adsorption}} \times \alpha_{ij}^{\text{diffusion}}$$

$\mathbf{D}_i$ and $\mathbf{D}_j$ are the self-diffusion coefficients of kind **i** and **j**. The membrane selectivity is the product of the adsorption selectivity and the diffusion selectivity.

Table 2 The adsorption selectivity, diffusion selectivity and membrane selectivity of the mixture N_2/NO_2 in ZIF materials at 10 bar at 373 K.

ZIF materials	Adsorption selectivity ($\boldsymbol{\alpha}_{ij}^{\text{adsorption}}$)	Diffusion selectivity ($\boldsymbol{\alpha}_{ij}^{\text{diffusion}}$)	Membrane selectivity ($\boldsymbol{\alpha}_{ij}^{\text{membrane}}$)
ZIF-8	4.5	1.15	5.2
ZIF-90	3.3	1.27	4.2
ZIF-78	6.0	1.77	10.6

1.2 Membrane separation of N_2O_4 from air at room temperature

In a mixture, containing only NO_2 and N_2O_4 at 1 bar and room temperature, the NO_2 content will be about 25 %. By lower pressure the NO_2/N_2O_4 equilibrium is shifted in favor of NO_2. But for the mixture N_2/NO_x the partial pressure of NO_x will be much smaller than 1 bar. Thus the ratio of NO_2 to N_2O_4 will be larger than 1:4. To assess this quantitatively, also the chemical reaction NO_2/N_2O_4 must be included.

The present work is, therefore, restricted to 373 K. One interesting aspect of the membrane selectivity at low and high temperature can, however, be considered without reaction simulations: We check in MD simulations with flexible lattice whether the bulky molecule N_2O_4 can diffuse within the ZIFs examined. If they cannot diffuse at 373 K, then the chance that they can diffuse at lower temperatures is zero. These considerations concerning a few isolated N_2O_4 molecules are independent of the composition of outside of the ZIF.

Figure 3 shows the time evolution of the MSD in the three materials, showing that N_2O_4 can neither penetrate nor diffuse in any of the ZIFs under study which indicates that no passage through such membranes should be possible. For the MD simulations, a few N_2O_4 molecules have been put into the cavities of the ZIFs. The space within the cavities is sufficient even if the molecules in cannot pass the windows to come to these positions. If NO_2 molecules had penetrated into these cavities, some N_2O_4 molecules could be formed there by dimerization. However, in the following the simulation can be considered as thought experiment independently of the source of N_2O_4 molecules in the cavity.

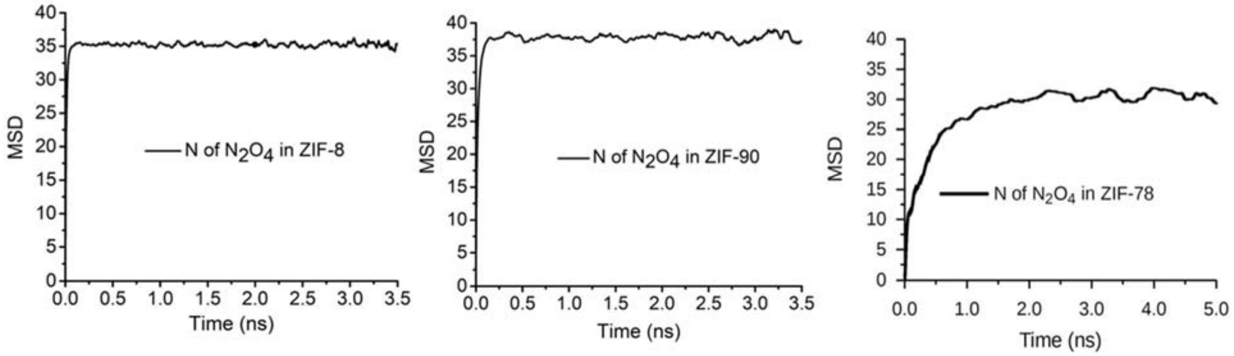


Fig. 3 The mean square displacement (MSD) of N atom in the N_2O_4 molecule for movements within the different ZIFs assuming flexible lattice.

Figure 3 clearly shows that the diffusion of N_2O_4 through the ZIFs under study is negligible. The slope of the MSD as a function of time vanishes (except fluctuations) before the square of the cavity diameter is reached. Thus, at 300 K where many NO_x are present as N_2O_4, a much higher membrane selectivity is to be expected than at 373 K, where the NO_x molecules mainly exist in form of NO_2.

1.3 Compared the adsorption selectivities in the Henry Law region and NO_2 Uptake at 1 bar

Table 3 compares the adsorption selectivities and NO_2 uptake at low pressure for the adsorption of N_2 and NO_2 in porous materials i.e. Zeolitic Imidazolate Frameworks-8, Zeolitic Imidazolate Frameworks-90, Zeolitic Imidazolate Framework-78 and Material of Institut Lavoisier-127.

Table 3 Adsorption selectivities and NO_2 Uptake at 1 bar and 298 K for 4 MOFs in the Henry Law Region.

MOF type	Selectivity $\mathbf{S}_{ij}$	NO_2 uptake at 1 bar and 298 K in mmol/g
ZIF-8	7,82	1,5
ZIF-90	7,59	5,4
ZIF-78	10,7	1,4
MIL-127	11,06	4,1

ZIF-90 is very similar to ZIF-8. The selecvity according to eq. (4) is $\mathbf{S}_{ij}$ = 7.59. MIL-127 has quite high uptake at 298 K and 1 bar and it has the highest adsorption selectivity at low pressure. ZIF-90 has even higher uptake but lower selectivity.

2. Investigating adsorption- and diffusion selectivity of CO_2 and CH_4 from Air on Zeolitic ImidazolateFramework-78 using molecular simulations

(Accepted by Microporous and Mesoporous Material, 274 (2019), 266-276.)

The ternary mixtures with $N_2/O_2/CO_2$ and $N_2/O_2/CH_4$ in Zeolitic Imidazolate Framework-78 are investigated by Gibbs ensemble Monte Carlo (GEMC) simulations for adsorption and by molecular dynamics (MD) simulations for diffusion. The adsorption and diffusion data are used for determining the membrane selectivities. N_2, O_2 ratios are found to be nearly the same in the gas and the adsorbed phase. At 228 K and low concentrations the CO_2/N_2 adsorption selectivity is found to attain values of as large as 140, further increasing with decreasing CO_2 concentration.

2.1 Parameter verification by simulated adsorption isotherms

Figure 4 (a) shows comparison of adsorption isotherms for CH_4, N_2, O_2 in ZIF-78 obtained from GEMC using different force fields compared with the experimental results from Banerjee et al. [2]. Parameters for N_2 and O_2 have been taken from Yang et al. [3]. They yield good agreement with the experiment of Banerjee et al. [2]. But, for CH_4 and CO_2 we could only find parameter sets that did not lead to an agreement with results of Banerjee et al. [2]. First we have compared isotherms from different parameter sets for CH_4. LS means that parameters from Liu and Smit [4] have been used. MH belongs to the parameters of Mendoza-Cortes et al. [5]. PS means the parameters taken from Prakash et al. [54]. VK means the TraPPE force field Martin and Siepmann [6] that was also used in Vlugt et al. [7], Hertag et al. [8]. Since no one of these parameter sets could be used to reproduce the experiment we had to modify one of them. TP means 'this paper'. We have chosen the widely accepted LJ diameter 3.73 Å of the TraPPE force field Martin and Siepmann [6].

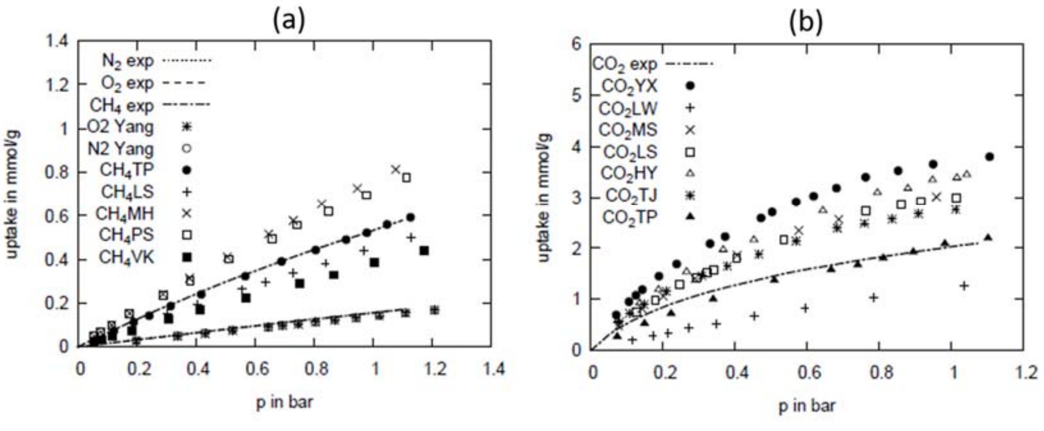


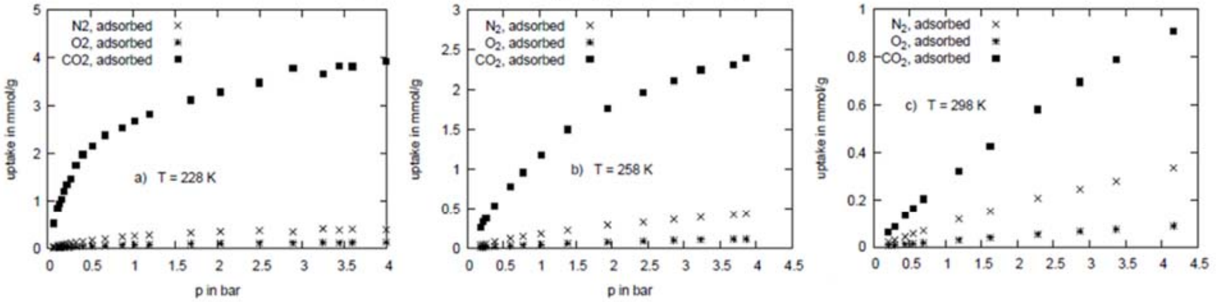
Fig. 4 Adsorption isotherms for single component in ZIF-78 obtained from GEMC using different force fields compared with the experimental results (a) CH_4, N_2, O_2 and (b) CO_2.

Figure 4 (b) shows a comparison of adsorption isotherms for CO_2 adsorption in ZIF-78 obtained from GEMC using different force fields with the experimental adsorption isotherm given in Banerjee et al. [2]. This isotherm has been measured only for the interval between 0 and about 1 bar. In all of the models compared here, CO_2 is modeled by a linear triatomic molecule with three LJ interaction sites. Point charges are located at these three LJ interaction sites to reproduce the quadrupole moment of CO_2. Model YX uses the TraPPE force field of Jeffrey et al. [9] for CO_2. The charges have been fitted to reproduce the vapor-liquid phase diagram of the binary mixture of CO_2/propane. These parameters have also been used in Yang et al. [10], Walton et al. [11]. The LW results have been obtained using parameters from Liu et al. [12] that is based on the LJ parameters of the UFF force field Rappe et al. [13]. The charges have been fitted to meet the first-order electrostatic and second-order conduction interaction. In Evanseck et al. [14] a parameter set is proposed that is named TJDM1 and compared with parameters that are reported to be derived from data given in Murthy et al. [15]. In Murthy et al. [15] the quadrupole moment is given but, no point charges. Hence, in Evanseck et al. [14] the point charges must have been fitted to meet the quadrupole moment of Murthy et al. [15]. These two parameter sets have been used in our curves TJ and MS, respectively. The LS model uses parameters from Liu and Smit [4]. These parameters are similar to that of the MS model. HY corresponds to parameters from Harris and Yung [16] that have also been used in the paper Zheng et al. [17]. Since no one of these isotherms agreed with the experiment for ZIF-78, we had to modify these parameters in this paper. In all of the mentioned papers the LJ parameters and the partial charges have been found by separate methods. Hence, it should be possible to combine them in different ways. We found after many trials that a combination of the UFF LJ parameters of Liu et al. [12] and the charges of Yang et al. [10] gave good agreement with the experiment for the CO2 adsorption and we used it in the present paper. TP means this paper. The adsorption isotherms at 298 K in named TP in Fig. 4 (a) and in Fig. 4 (b) for the pure substances N_2, O_2, CO_2 and CH_4 show good agreement with the experimental data reported in ref. Banerjee et al. [2]. Thus it is promising to use these parameters for the investigation of also structure, diffusion and mixture properties.

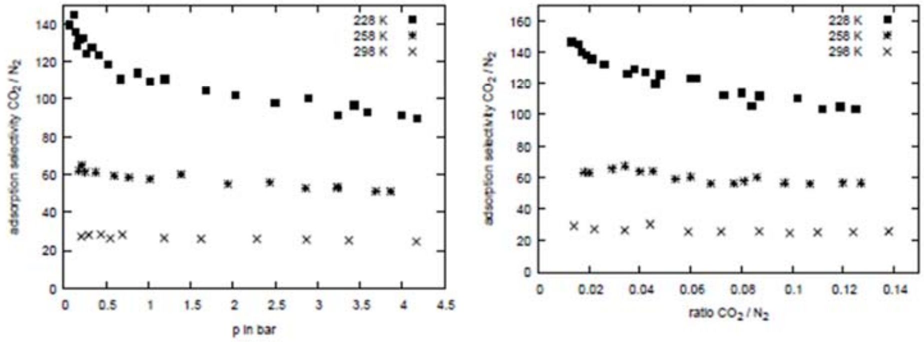
Most interestingly, for all pressures considered the ratio of the amounts of N_2 and O_2 are found to be almost equal in the adsorbed and gaseous phases. With these adsorption properties, air behaves as if it would be one component. But, this is a result of our research and could not be assumed in advance without prove.

2.2 CO_2 and CH_4 in air by simulated adsorption isotherms

Fig. 5 (a) shows the uptake of the three gases as a function of the pressure for three different temperatures. Note, that the pressure in Fig. 5 is the final equilibrium pressure of the equilibrium composition in the gas box. In contrast to CO_2 the amount of adsorbed molecules of types N_2 and O_2 seems to be far from saturation, even in the mixture when CO_2 is filling some space in the cavities. Hence, the selectivity is expected to become smaller if the pressure is increased up to e.g. 6-10 bar which is the pressure usually used in technical pressure swing adsorption.



(a) Adsorption $N_2/O_2/CO_2$ at 228, 258 and 298 K



(b) Adsorption selectivity $N_2/O_2/CO_2$ at 228, 258 and 298 K

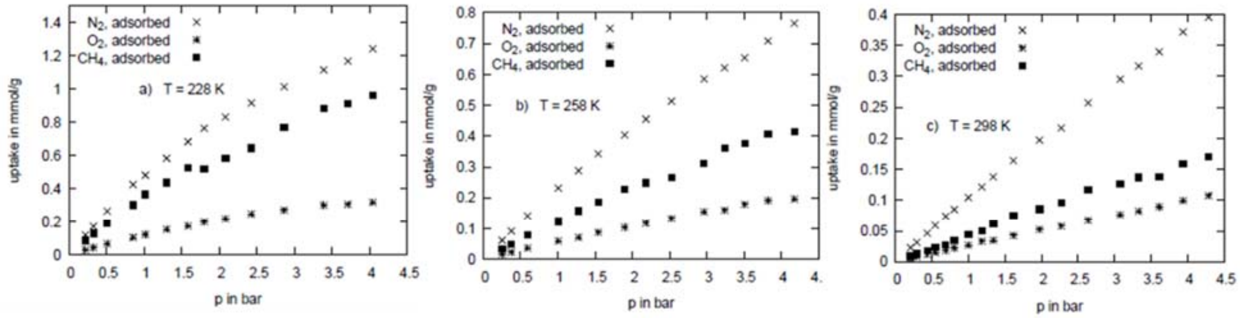
Fig. 5 Adsorption and Adsorption selectivity for the CO_2/air mixture at different temperatures.

Figure 5 (b) shows the CO_2/N_2 adsorption selectivity in the ternary mixture $CO_2/N_2/O_2$ as a function of the pressure (left hand side). The concentration dependence of the selectivity at different temperatures and constant pressure of 1 bar can be seen on the right hand side of Figure 5 (b). The CO_2 / N_2 adsorption selectivity in the ternary mixture at 228 K at low pressures reaches values of more than 140. It depends strongly upon temperature and pressure. The pressure dependence at higher temperatures is less pronounced.

Interestingly, figure 5 shows that a decrease of the temperature increases the adsorption selectivity drastically. Therefore, a temperature swing method for separation processes appears to be attractive. Because also a decrease of the pressure increases the selectivity, a simple decompression of the feed gas, that leads to both a lower temperature and pressure, might be a promising way towards selectivity enhancement.

In figure 6 (a) the adsorption isotherms for a mixture CH4/air are given. The preparation of the system and the technical details were the same as described in the case of CO2.

(a) Adsorption $N_2/O_2/CH_4$ at 228, 258 and 298 K



(b) Adsorption selectivity $N_2/O_2/CH_4$ at 228, 258 and 298 K

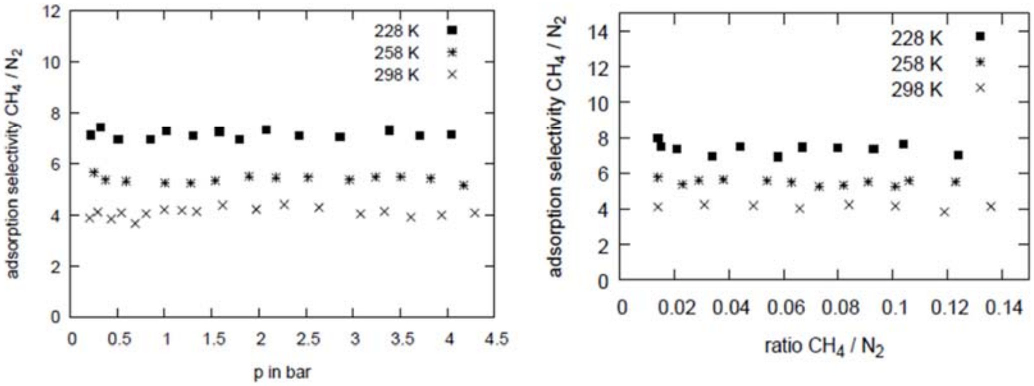


Fig. 6 Adsorption and Adsorption selectivity for the CH_4/air mixture at different temperatures.

In figure 6 (b) shows the adsorption selectivity for CH_4/N_2 in the ternary $CH_4/ N_2/O_2$ mixture at different temperatures for a ratio of 0.1 of CH_4 to N2 molecules and of the concentration of CH_4 at 1 bar, also at different temperatures. In contrary to CO2 adsorption the concentration dependence of the CH_4/N_2 selectivity in air is quite small.

2.3 CH_4 in Self-diffusion Coeffcients (Ds) from MD and Membrane Selectivities

Mean square displacements (MSDs) of the molecules are evaluated and self-diffusion coefficients (Ds) are obtained from the slope of linear fits of the MSDs. The Ds resulting from MD simulations in the rigid lattice of 4x4x4 unit cells of ZIF-78 are given in Table 4. As pointed out in the computational details the small guest particle numbers make it difficult to calculate reliable self-diffusion coefficients (Ds) even in the big system of 4x4x4 unit cells (41,472 lattice atoms). Each long trajectory is just sufficient to calculate one Ds value and therefore error bars cannot be obtained. A tentative estimation basing on the shape of the MSDs would be that the error can be about 20 %.

Interestingly, the results in Table 4 show that although the self-diffusion coefficients of CH_4 and CO_2 are not very different in their corresponding mixtures, the self-diffusion coefficients of N_2 and O_2 are significantly smaller in the mixture with CO_2. This may be explained by the larger number of adsorbed CO_2 that leads to hindrance of the motion of N_2 and O_2.

Table 4 Self-diffusion coefficients (resulting under the rigid-lattice approximation) in the ternary mixtures of CH_4 and CO_2 with air (i.e. N_2 and O_2) in ZIF-78 with a ration of the molecule numbers CH_4/N_2 and CO_2/N_2.

Guest molecule	Self-diffusion coefficients (m^2/sec)		
	228 K	258 K	298 K
$CH_4/N_2/O_2$			
CH_4	$0.32x10^{-10}$	$0.51x10^{-10}$	$0.89x10^{-10}$
N_2	$0.70x10^{-10}$	$1.17x10^{-10}$	$1.89x10^{-10}$
O_2	$1.10x10^{-10}$	$1.96x10^{-10}$	$4.10x10^{-10}$
$CO_2/N_2/O_2$			
CO_2	$0.32x10^{-10}$	$0.482x10^{-10}$	$0.81x10^{-10}$
N_2	$0.48x10^{-10}$	$0.70x10^{-10}$	$1.94x10^{-10}$
O_2	$0.68x10^{-10}$	$1.93x10^{-10}$	$4.12x10^{-10}$

The membrane selectivity can be calculated from the adsorption selectivity and the diffusion selectivity. Table 5 summarizes the thus determined data.

Table 5 Selectivities of CH_4/air and CO_2/air. membrane selectivity = diffusion selectivity x adsorption selectivity in ZIF-78 with a ratio of 0.1 of the molecule numbers CH_4/N_2 and CO_2/N_2, respectively.

Selectivity	Temperature		
	228 K	258 K	298 K
$CH_4/N_2/O_2$			
Diffusion selectivity	0.45	0.43	0.47
Adsorption selectivity	5.65	4.56	3.52
Membrane selectivity	2.54	1.96	1.65
$CO_2/N_2/O_2$			
Diffusion selectivity	0.67	0.68	0.42
Adsorption selectivity	90.30	62.90	31.70
Membrane selectivity	60.50	42.77	13.31

The membrane selectivity CH_4/N_2 is about 2.54. The membrane selectivity CO_2/N_2 is around 60.5 at 228 K, 42.77 at 258 K and 13.31 at 298 K. Therefore, the separation of CO2 from air, techniques based on adsorption appear to be more promising than those based on membrane separation, the more since they operate even for high dilution more effectively than for higher pollution. For the separation of CH4/air mixtures, techniques based on adsorption and techniques based on permeation seem to work both with moderate selectivity.

3. Molecular Simulations of a CO_2/CO Mixture in MIL-127

(Accepted by Chemical Physics Letters, 696 (2018), 86-91.)

The strategy of this part is the following: First, reliable interaction parameters must be found. This is not easy because generally accepted parameters for the guest–host interaction do not exist for (Metal Organic Frameworks) MOFs. In contrary, it turned out that parameters that have been used successfully for a given MOF, failed to work well for the same guest molecules in another MOF. therefore, we first compared adsorption isotherms from Gibb Ensemble Monte Carlo (GEMC) simulations of single gas adsorption using different parameter sets of other simulation papers with measured adsorption isotherms. The parameters that turned out to be suitable in describing the single component adsorption isotherm for the present system have then be used to simulate the mixture adsorption isotherms and for Molecular Dynamics (MD) simulations.

3.1 Parameters for the guest–host interaction

The GEMC simulations have been carried out by a home-made software called Gibbon that was used in [18,19,20]. The charges have been treated by a kind of charge groups model similar to that of [12] as it has been applied and explained already in [18]. The basic idea is that the sum of Coulomb potential contributions of the partial charges of the molecules CO_2 or CO to the interaction with another charge (**e.g.** with the partial charge of a lattice atom) decays for large distances much faster than the single contributions. Thus the computer time extensive Ewald summation can be avoided in the GEMC simulations. The interaction parameters for CO have been taken from John E. Straub et al. [21]. The parameters for CO_2 and for the lattice of MIL-127 are the ones that have been tested, used and described in [18].

Figure 7 shows a comparison of GEMC simulations for pure CO in MIL-127(Fe), using these parameters, compared with the measured adsorption isotherm of [22].

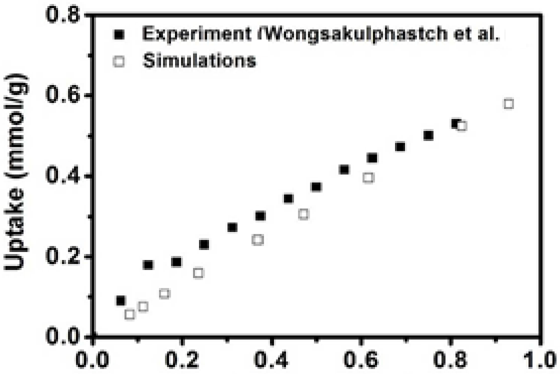


Fig. 7 Adsorption isotherm of CO at 303 K in MIL-127(Fe)

3.2 Gibb Ensemble Monte Carlo (GEMC) simulations

Figure 8 (a) shows the adsorption isotherms of CO_2/CO mixtures for three different temperatures. The adsorption of CO is much smaller than that of CO_2 because of the quadrupole moment of CO_2. Remarkably, that also the temperature dependence of the CO adsorption is very small. Interestingly, the number of adsorbed CO molecules in the mixture adsorption simulation increases slightly with increasing temperature what is contra intuitive and can be explained by the strong concurrency of the CO_2 and CO molecules in occupying the favorite adsorption sites.

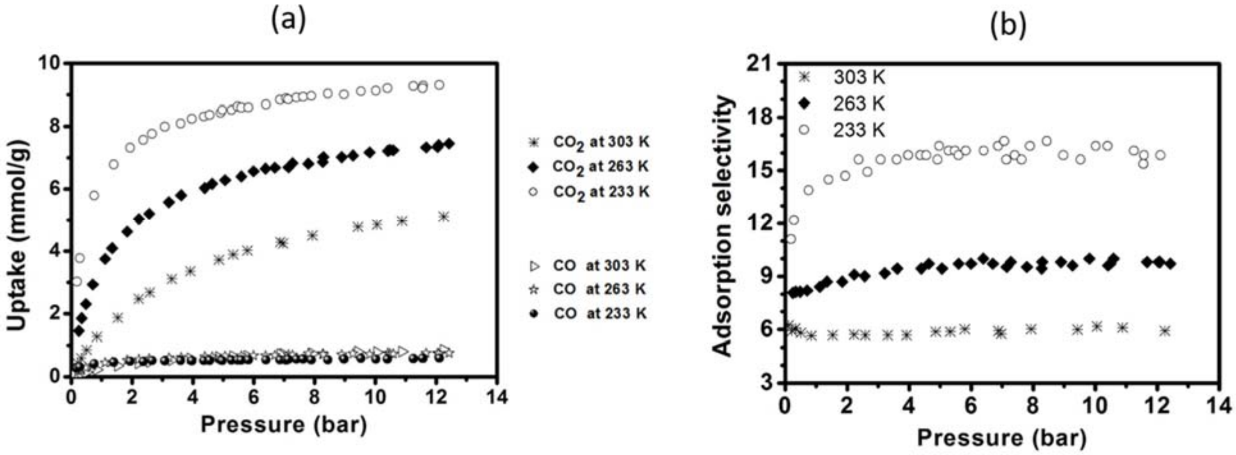


Fig. 8 (a) Adsorption isotherms (b) Adsorption selectivity of CO_2/CO mixtures on MIL-127(Fe) for three different temperatures.

It follows from the above mentioned results that the adsorption selectivity as shown in figure 8 (b) that shows a strong temperature dependence. The pressure region 1 to 10 bar has been chosen for the simulations because this is the technically interesting interval for pressure swing adsorption. Moreover, the CO_2 adsorption at 12 bar is not very far from the saturation. Therefore, it cannot be expected that higher pressure would increase the adsorption selectivity considerably. It can also be seen from figure 8 (a) that in pressure swing adsorption the lower pressure for the desorption should be lower than 1 bar since the adsorption of CO_2 is already quite strong at 1 bar.

At the temperature of 233 K instead of room temperature, the adsorption selectivity can be increased from about 6 to about 15. Hence, MIL-127 seems to be well suited to serve as an adsorbent for pressure swing adsorption for the separation of CO_2 from CO. Particularly promising is the adsorption at low temperature and a pressure above about 6 bar and the desorption at higher temperature and a pressure below 0.5 bar.

3.2. Molecular Dynamics Simulations (MD)

The MD simulations have been done by the DL_POLY software [22]. Ewald summation was done in the MD simulations, because DL_POLY does not offer the possibility of a charge group treatment. The adsorbed gas mixture was investigated in order to find adsorption sites and to check if a kind of clustering between adsorbed particles can be observed. The particle numbers for the MD simulations of adsorbed particles in the MIL have been taken from the results of the GEMC simulations at about 12 bar. These particle numbers are: 251 CO_2 and 42 CO at 303 K, 361 CO_2 and 37 CO at 263 K and 453 CO_2 and 29 CO at 233 K, respectively.

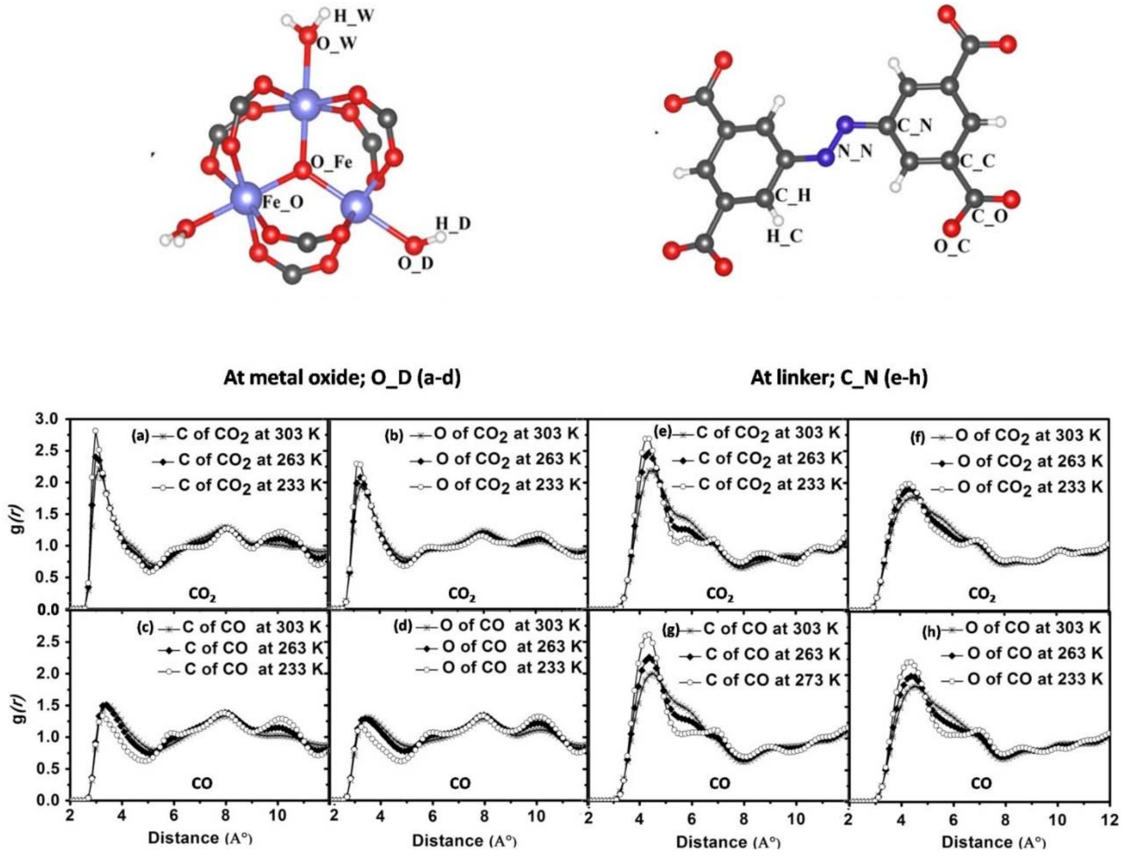


Fig. 9 Radial Distribution Functions (RDF) of the CO_2/CO mixture and atom type O_D in MIL-127(Fe) (a,b,c,d) and atom type C_N (e,f,g,h) for three temperatures.

Figure 9 shows RDFs between the guest molecules CO_2 and CO with the two most important adsorption sites at the O_D and C_N atoms of the lattice. The meaning of O_D and C_N is explained by the structure picture. The most important first peak is situated at distances of about 3 Å for the RDF O_D Fig.5(a) that roughly correspond to the atom diameters of C and O and for C_N around 4 Å figure 9 (e). That means that the adsorption center is direct at the corresponding lattice atom.

Figure 10 shows the RDFs between CO_2-CO_2 and CO_2-CO. Interestingly, the peak of the RDF between the C atoms of different CO_2 molecules is approximately as high as the peak with the two adsorption centers at the lattice. That means that there is really a strong correlation between their positions that may explain that they can form clusters of 2 or more CO_2 and their formation and destruction can be a reason for sudden changes in apparent equilibrium situations as observed in the adsorption simulations.

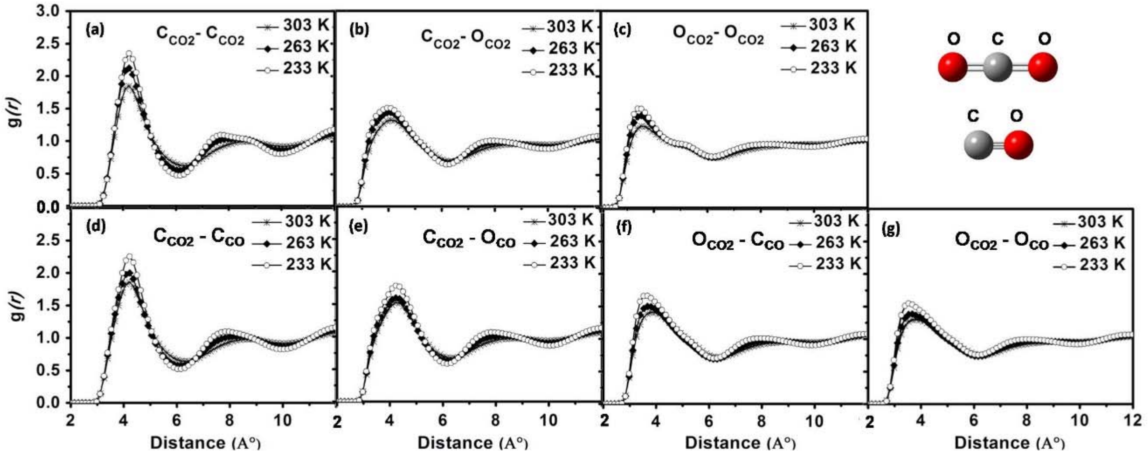


Fig. 10 Radial Distribution Functions (RDF) between CO_2 and CO mixture in MIL-127(Fe) for three temperatures.

The C-C RDFs of CO_2-CO_2 show higher peaks than the C-O RDFs or O-O RDFs. That means that the favorite arrangement is that the C atoms are close together in spite of their equal partial charge. Maybe, the reason can be that both CO_2 in such situations are close to an adsorption center of the lattice. For such pairs of CO_2 no favorite position of their oxygen atoms (as it would be an parallel arrangement of the two CO_2) seems to exist because the C-O and O-O RDFs are not very different from 1. Also the RDF between the C from CO_2 and the C from CO shows a quite high peak. RDFs between CO and CO molecules are given in the supporting data because the peak is not high (only close to 1).

The MD simulations are used to calculate the self-diffusion coefficients using the Einstein relation. The two self-diffusion coefficients D_s of CO_2 and CO in their binary mixture adsorbed in Co-MIL-127(Fe) are not very different and show an exponential temperature dependence as can be seen in Table 6.

Table 6 The Self-diffusion coefficients (**D_s**) of CO_2 and CO in the binary CO_2/CO mixture in MIL-127(Fe) for three different temperatures. At 303 K = 251CO_2/42CO, 263K = 361CO_2/37CO and 223 K = 453CO_2/29CO molecule/8unit cells

T (K)	Pressure (bar)	**Ds** of CO_2 (m^2/sec)	**Ds** of CO (m^2/sec)
303	12.20	10.5×10^{-10}	11.5×10^{-10}
263	12.04	3.7×10^{-10}	4.7×10^{-10}
233	11.55	1.8×10^{-10}	2.4×10^{-10}

3.3 Adsorption, diffusion and membrane selectivities

The effectivity of separation processes can be expressed by the selectivities. Table 6 shows the different selectivities as obtained from the simulations. The selectivities have been calculated with the numbers of adsorbed particles from the GEMC simulations. The pressure is the equilibrium pressure of the GEMC simulations. It has been calculated from the densities that result from the simulations by the Peng-Robinson equation of state. The pressures are around 12 bar but somewhat different. The reason is that the resulting equilibrium pressure of a simulation cannot be predicted at the beginning of a simulation. It could have been adjusted by trial and error in additional simulations, but we believe that the results are clear enough also in this way.

Table 7 The adsorption selectivity, diffusion selectivity and membrane selectivity of the CO_2/CO mixture in MIL-127(Fe)

T (K)	Pressure (bar)	Adsorption selectivity ($\alpha_{ij}^{adsorption}$)	Diffusion selectivity ($\alpha_{ij}^{diffusion}$)	Membrane selectivity ($\alpha_{ij}^{membrane}$)
303	12.20	5.92	0.91	5.40
263	12.04	9.80	0.77	7.57
233	11.55	15.38	0.77	11.80

From the results of Table 7 we can predict that MIL-127(Fe) is well suited to separate CO_2 from CO. As expected, the separation is more effective at lower temperature. The adsorption selectivity is somewhat larger than the membrane selectivity. Finally, it can be concluded that MIL-127(Fe) is well suited to separate CO_2 from CO, especially at lower temperature. The adsorption selectivity is somewhat larger than the membrane selectivity.

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Output of the research

Publications

1. T. Chokbunpiam, S. Fritzsche, V. Parasuk, J. Caro, S. Assabumrungrat "Molecular simulations of a CO_2/CO mixture in MIL-127" Chemical Physics Letters, 696 (2018), 86-91.
2. R. Chanajaree, T. Chokbunpiam, J. Kärger, S. Hannongbua, S. Fritzsche, "Investigating adsorption- and diffusion selectivity of CO_2 and CH_4 from air, on zeolitic imidazolate Framework-78 using molecular simulations", Microporous and Mesoporous Materials 274, (2019), 266-276.
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4. T. Ploymeerusmee, S. Fritzsche, S. Hannongbua, T. Chokbunpiam,"CO_2 induced swing effect at imidazolate of zeolitic imidazolate framework-90 using molecular simulations", Theoretical Chemistry Accounts, 138 (118), (2019), 1-7.

Conferences

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2. T. Chokbunpiam, T. Ploymeerusmee, S. Fritzsche, S. Hannongbua, "The effect of temperature and CO_2 loading on structural and dynamical properties of Zeolitic Imidazolate Frameworks", The 2nd Taiwan-Thailand-Vietnam Workshop on Theoretical and Computational Chemistry (TTV 2), Science Park, Pathum Thani, Thailand (January 17-20, 2019)
3. T. Chokbunpiam, S. Fritzsche J. Caro, S. Hannongbua, W. Janke, T. Remsungnen, "Extraordinary adsorption/reaction selectivity of NO_x from N_2 by combined adsorption and reaction on MIL-127", Computational Physics Group, Institut f¨ur Theoretische Physik, Universit¨at Leipzig, Germany, (November 28-30, 2019)
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APPENDIX

PUBLICATIONS

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Research paper

Molecular simulations of a CO_2/CO mixture in MIL-127

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ABSTRACT

Adsorption and diffusion of an equimolar feed mixture of CO_2 and CO in MIL-127 at three different temperatures and pressures up to 12 bar were investigated by molecular simulations. The adsorption was simulated using Gibbs-Ensemble Monte Carlo (GEMC). The structure of the adsorbed phase and the diffusion in the MIL were investigated using Molecular Dynamics (MD) simulations. The adsorption selectivity of MIL-127 for CO_2 over CO at 233 K was about 15. When combining adsorption and diffusion selectivities, a membrane selectivity of about 12 is predicted. For higher temperatures, both adsorption and diffusion selectivity are found to be smaller.

1. Introduction

Gas storage, adsorption or catalysis need surface-rich porous materials with narrow pore size distribution in the nm region. Zeolites, MCMs and metal-organic frameworks (MOFs) are examples for crystalline nanoporous materials. MOFs consist of metal ions or metal oxide clusters, that are connected by organic molecules, called linkers. Metal ions/oxide clusters and organic linkers can be replaced by other metal ions and other linkers forming the huge variety of possible MOF materials. They even can be tailored to special applications [1].

One important application of MOFs is the separation of gases from mixtures [2]. Crucial for potential applications of MOFs for storage or separation purposes are adsorption at the internal surface and diffusion along pores and channels. These phenomena are therefore examined by numerous experimental measurements and computer simulations (see overviews in [2,3,4]).

Particularly computer simulations can give a fast estimation which MOFs that are suited for which separations. *E.g.* in Haldoupis et al. [4] 504 MOF structures are tested by computer simulations with rigid MOF frameworks in order to find such answers. This gives a valuable practical tool to experimentalists and industrial users even if, in cases where diameters of apertures and guest molecules are of similar size, more refined investigations are needed [5] to take into account the flexibility of MOF lattices.

One of the MOF materials has been synthesized as Material Institut Lavoisier - 127 (MIL-127) [6]. It is a stable rather rigid porous crystal that consists of Fe^{3+} cations interconnected by 3,3′,5,5′-azobenzenetetracarboxylate anions. Its three dimensional pore structure with diameters of 5–7 Å contains hydrophilic and hydrophobic groups and exhibits two types of pores including a system of channels connecting cages of around 10 Å diameter. Because of these structural properties MIL-127 seems to be well suited for storage and separation purposes. The wide pores could even be used for drug encapsulation and drug delivery because this MIL material is biocompatible [7]. It is also an interesting candidate for use as a catalyst [8].

CO_2 and CO are prominent members among the gases that pollute air. They are formed by burning fossil fuels and in many industrial processes. Particularly CO is toxic and flammable while CO_2 as greenhouse gas can be recovered, stored ore reused. Therefore, the

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separation of the two gases in mixtures is desirable. Single gas adsorption isotherms of CO and CO_2 sorption in both MIL-127 (Fe^{3+}) and mixed metal (iron(III) and another metal(II) of MIL-127 have recently been measured [9]. To our knowledge no experimental papers except the mentioned ones are available for the system under consideration.

In [10] the adsorption and diffusion of carbon dioxide in MIL-127(Fe) was examined by computer simulations including Molecular Dynamics (MD) and Gibbs Ensemble Monte Carlo (GEMC) studies. Both methods are well known and have been also used before by our group in several papers [10,11,12] and described there in details. Additional information is also given in supporting material. Gibbs Ensemble Monte Carlo (GEMC) simulations [13] are essentially Metropolis Monte Carlo simulations carried out simultaneously in two systems, a gas phase and an adsorbed phase within a porous solid. By well-defined particle exchange between the two systems, equilibrium is established. Thus, an adsorption equilibrium between a gas phase and an adsorbed phase can be simulated without knowing a value for the chemical potential as an input quantity as this would be the case in GCMC. Of course, all Monte Carlo methods finally rely on acceptance probabilities that are implicitly based on the chemical potential. But, only in GCMC this is an explicit input quantity. The pressure (needed only for comparison with experiments or with other simulation papers) can easily be calculated from the density by an equation of state in the gas phase. For pressures of around 1 bar, even the ideal gas equation of state is sufficient. For higher pressure the Peng-Robinson equation of state [14] can be used. The chemical potential can be evaluated by Widoms method [15] in order to have an additional check for the equilibrium because the chemical potential for each sort of guest molecules must be equal in both phases in equilibrium. This additional check is useful but not needed for the GEMC simulation.

The classical MD simulations of this paper consist of solving numerically the Newtons equations for several thousands of particles in order to calculate the trajectories of the particles. These trajectories are then examined by statistical methods [15,16].

It has been shown that diffusion of guest molecules in several ZIF materials [5,17], and also in the MOF Zn(tbip) [18] can be strongly influenced by the lattice flexibility in cases where the size of the guest molecules and the diameters of channels or apertures of the cavities are of approximately equal size. In [10] it could be shown that this is not the case for CO_2 (3.3 Å) and CO (3.8 Å) in MIL-127 (5...7 Å). Hence, the simulations reported in this paper could be carried out with rigid framework. This assumption of a rigid framework is in complete accordance with [19] where also MIL-127(Fe) was investigated.

The strategy of the present paper is the following: First, reliable interaction parameters must be found. This is not easy because generally accepted parameters for the guest – host interaction do not exist for MOFs. In contrary, it turned out that parameters that have been used successfully for a given MOF, failed to work well for the same guest molecules in another MOF.

Therefore, we first compared adsorption isotherms from GEMC simulations of single gas adsorption using different parameter sets of other simulation papers with measured adsorption isotherms. The parameters that turned out to be suitable in describing the single component adsorption isotherm for the present system have then be used to simulate the mixture adsorption isotherms and for MD simulations.

2. Details of the simulations

The GEMC simulations have been carried out by a home-made software called Gibbon that was used in [10–12]. The charges have been treated by a kind of charge groups model similar to that of [20] as it has been applied and explained already in [10]. The basic idea is that the sum of Coulomb potential contributions of the partial charges of the molecules CO_2 or CO to the interaction with another charge (*e.g.* with the partial charge of a lattice atom) decays for large distances much faster than the single contributions. Thus the computer time extensive Ewald summation can be avoided in the GEMC simulations. Such methods came recently into the focus of scientists doing many particle computer simulations [21]. The MD simulations have been done by the DL_POLY software [22]. Ewald summation was done in the MD simulations, because DL_POLY does not offer the possibility of a charge group treatment.

The interaction parameters for CO have been taken from Straub et al. [23]. Fig. 1 shows a comparison of our simulations (GEMC) for pure CO in MIL-127(Fe), using these parameters, compared with the measured adsorption isotherm of [9]. The parameters for CO_2 and for the lattice of MIL-127 are the ones that have been tested, used and described in [10]. Tables T1–T3 summarizing all interaction parameters are given in supporting material.

Please note, that the interaction parameters of lattice atoms depend on the chemical bonds to other lattice atoms in the neighborhood. Therefore, we introduced different atom types (*e.g.* C_O and C_N for carbon depending upon the neighbors) that can be seen in Fig. 2.

It should be added that particularly the CO_2 adsorption showed big fluctuations that made simulations up to 300 millions of GEMC simulation steps necessary. This big computational effort is the reason why screening of several materials or of many different mixture compositions would hardly be possible.

The simulations of this paper have been done for an equimolar gas mixture that leads of course to another ratio in the adsorbed phase.

The particle numbers of 2000–3000 for both CO_2 and CO have been used in the GEMC simulations at 233 K. These numbers are different in different runs because the non-equimolar ratios in the gas phase from the runs, have been adjusted to equimolar ratios by removal of particles of one sort and new equilibration of the system. Quite long runs are necessary in order to distinguish between (i) fluctuations around an equimolar state, and (ii) real differences from an average equimolar state. This also increases the computational effort considerably.

The particle numbers for the MD simulations of adsorbed particles in the MIL have been taken from the results of the GEMC simulations at about 12 bar. These particle numbers are: 251 CO_2 and 42 CO at 303 K, 361 CO_2 and 37 CO at 263 K and 453 CO_2 and 29 CO at 233 K, respectively.

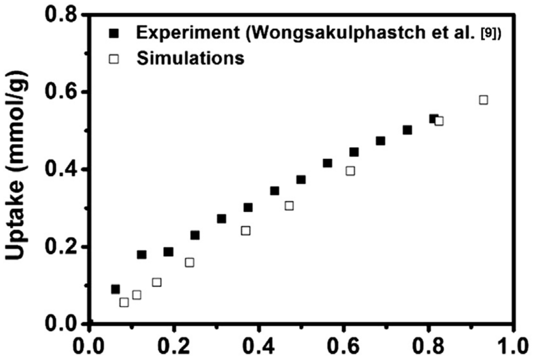

Fig. 1. Adsorption isotherm of CO at 303 K in MIL-127(Fe).

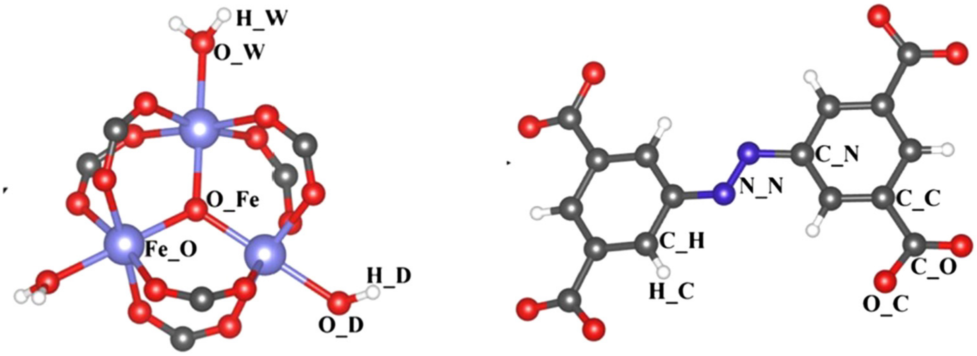

Fig. 2. Atom types in MIL-127.

3. Results and discussions

3.1. Adsorption isotherms of CO_2/CO mixtures for three different temperatures

Fig. 3 shows the adsorption isotherms of CO_2/CO mixtures for three different temperatures. The adsorption of CO is much smaller than that of CO_2 because of the quadrupole moment of CO_2. Remarkably, that also the temperature dependence of the CO adsorption is very small. Interestingly, the number of adsorbed CO molecules in the mixture adsorption simulation increases slightly with increasing temperature what is contra intuitive and can be explained by the strong concurrency of the CO_2 and CO molecules in occupying the favorite adsorption sites.

It follows from the above mentioned results that the adsorption selectivity as shown in Fig. 4 shows a strong temperature dependence.

The pressure region 1–10 bar has been chosen for the simulations because this is the technically interesting interval for pressure swing adsorption. Moreover, the CO_2 adsorption at 12 bar is not very far from the saturation. Therefore, it cannot be expected that higher pressure would increase the adsorption selectivity considerably. It can also be seen from Fig. 3 that in pressure swing adsorption the lower pressure for the desorption should be lower than 1 bar since the adsorption of CO_2 is already quite strong at 1 bar.

At the temperature of 233 K instead of room temperature, the adsorption selectivity can be increased from about 6 to about 15. Hence, MIL-127 seems to be well suited to serve as an adsorbent for pressure swing adsorption for the separation of CO_2 from CO.

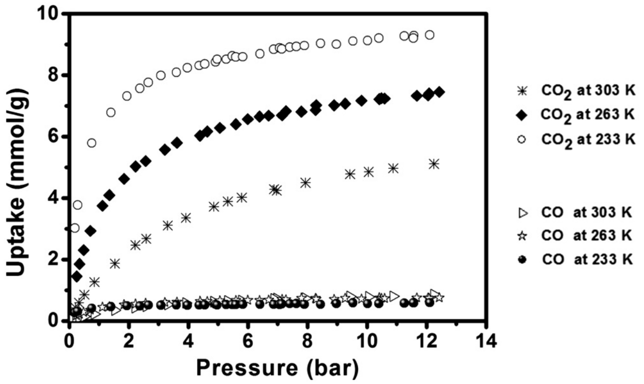

Fig. 3. Adsorption isotherms of CO_2/CO mixtures on MIL-127(Fe) for three different temperatures.

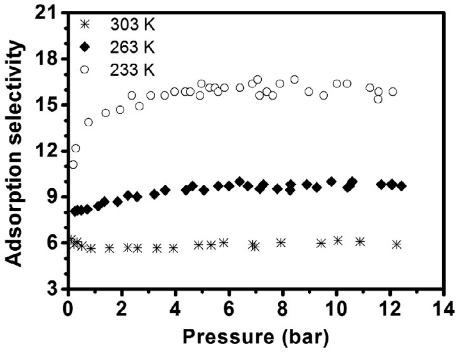

Fig. 4. Adsorption selectivity of CO_2/CO mixtures in MIL-127(Fe) for three different temperatures.

Particularly promising is the adsorption at low temperature and a pressure above about 6 bar and the desorption at higher temperature and a pressure below 0.5 bar.

3.2. Molecular Dynamics simulations (MD)

In the MD simulations first the structure of the adsorbed gas mixture was investigated in order to find adsorption sites and to check if a kind of clustering between adsorbed particles can be observed. Such cooperative phenomena could explain the big fluctuations observed in the simulations of adsorption uptake. If namely clusters are formed that decompose from time to time, then big fluctuations in the structure and hence in the adsorption can be understood. The structure investigation has been done by the Radial Distribution Functions (RDFs) [10].

The MD simulations are used to calculate the self-diffusion coefficients using the Einstein relation that is valid for large τ.

$$\langle|\vec{r}(\tau)-\vec{r}(0)|^2\rangle = \frac{1}{N}\sum_{j=1}^{N}\left(\vec{r}_j(\tau)-\vec{r}_j(0)\right)^2 = 6D_s\tau$$

In this formula ($\vec{r}(\tau)$ and $\vec{r}(0)$ mean the position vectors of a particle at time $t = \tau$. d $t = 0$, respectively. The quantity on the left hand side of the equation is called the Mean Square Displacement (MSD).

3.2.1. Radial Distribution Functions (RDF) of CO_2/CO mixture at preferential adsorption sites O_D and C_N in MIL-127(Fe)

Fig. 5 shows RDFs between the guest molecules CO_2 and CO with the two most important adsorption sites at the O_D and C_N atoms of the lattice. The meaning of O_D and C_N is explained by the structure picture. The most important first peak is situated

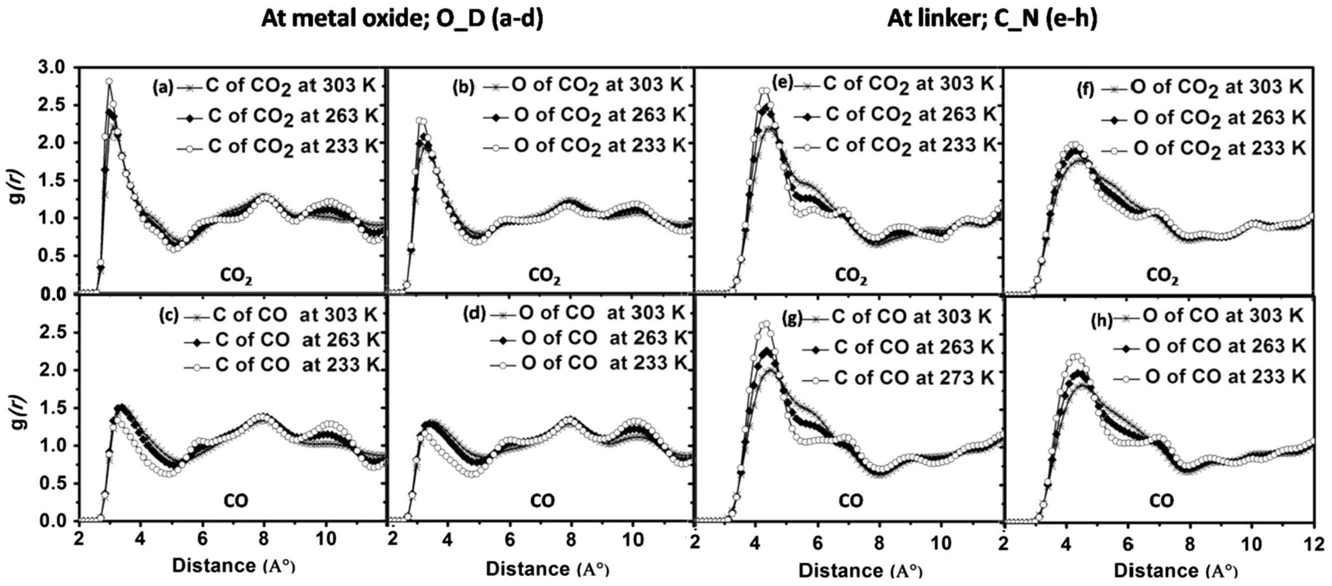

Fig. 5. Radial Distribution Functions (RDF) of the CO_2/CO mixture and atom type O_D in MIL-127(Fe) (a–d) and atom type C_N (e–h) for three temperatures.

at distances of about 3 Å for the RDF O_D Fig. 5(a) that roughly correspond to the atom diameters of C and O and for C_N around 4 Å Fig. 5(e). That means that the adsorption center is direct at the corresponding lattice atom.

The RDFs between the CO_2 and CO and all other atom types in MIL-127(Fe) are shown in the supporting data.

3.2.2. Radial Distribution Functions (RDF) between CO_2/CO molecules in MIL-127(Fe)

Fig. 6 shows the RDFs between CO_2-CO_2 and CO_2-CO. Interestingly, the peak of the RDF between the C atoms of different CO_2 molecules is approximately as high as the peak with the two adsorption centers at the lattice. That means that there is really a strong correlation between their positions that may explain that they can form clusters of 2 or more CO_2 and their formation and destruction can be a reason for sudden changes in apparent equilibrium situations as observed in the adsorption simulations.

The C-C RDFs of CO_2-CO_2 show higher peaks than the C-O RDFs or O-O RDFs. That means that the favorite arrangement is that the C atoms are close together in spite of their equal partial charge. Maybe, the reason can be that both CO_2 in such situations are close to an adsorption center of the lattice. For such pairs of CO_2 no favorite position of their oxygen atoms (as it would be an parallel arrangement of the two CO_2) seems to exist because the C-O and O-O RDFs are not very different from 1.

Also the RDF between the C from CO_2 and the C from CO shows a quite high peak.

RDFs between CO and CO molecules are given in the supporting data because the peak is not high (only close to 1).

Table 1
The Self-diffusion coefficients (D_s) of CO_2 and CO in the binary CO_2/CO mixture in MIL-127(Fe) for three different temperatures. At 303 K = 251CO_2/42CO, 263 K = 361CO_2/37CO and 223 K = 453CO_2/29CO molecule/8unit cells.

T (K)	Pressure (bar)	*Ds.* of CO_2 (m^2/s)	*Ds.* of CO (m^2/s)
303	12.20	10.5×10^{-10}	11.5×10^{-10}
263	12.04	3.7×10^{-10}	4.7×10^{-10}
233	11.55	1.8×10^{-10}	2.4×10^{-10}

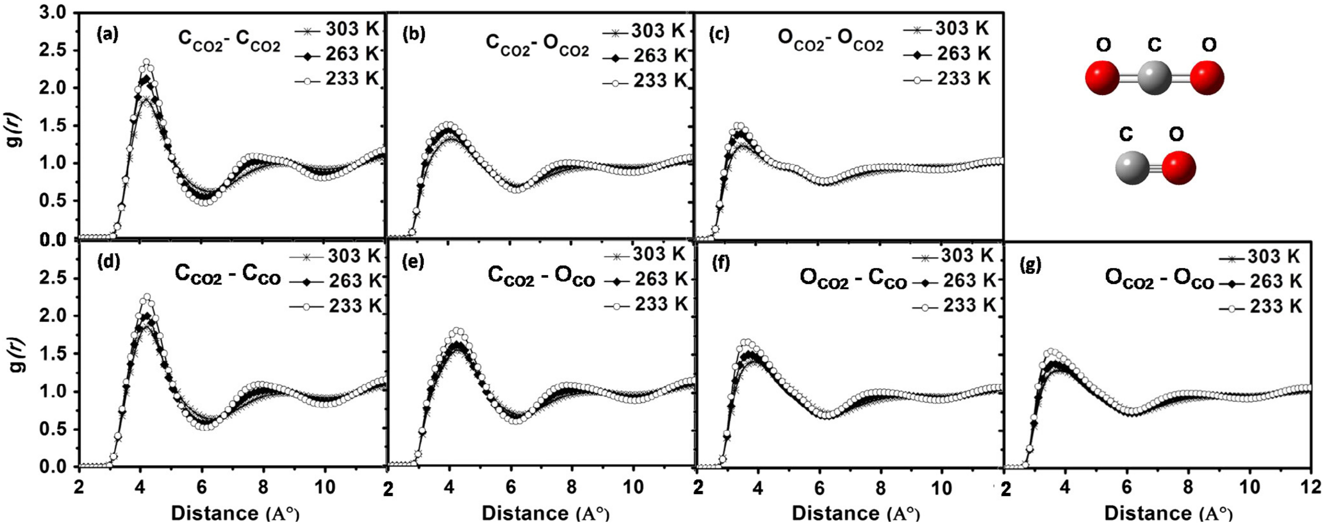

Fig. 6. Radial Distribution Functions (RDF) between CO_2 and CO mixture in MIL-127(Fe) for three temperatures.

Table 2
The adsorption selectivity, diffusion selectivity and membrane selectivity of the CO_2/CO mixture in MIL-127(Fe).

T (K)	Pressure (bar)	Adsorption selectivity ($\alpha_{ij}^{adsorption}$)	Diffusion selectivity ($\alpha_{ij}^{diffusion}$)	Membrane selectivity ($\alpha_{ij}^{membrane}$)
303	12.20	5.92	0.91	5.40
263	12.04	9.80	0.77	7.57
233	11.55	15.38	0.77	11.80

3.2.3. Diffusion coefficients

The two self-diffusion coefficients D_s of CO_2 and CO in their binary mixture adsorbed in Co-MIL-127(Fe) are not very different and show an exponential temperature dependence as can be seen in Table 1.

3.2.4. Adsorption, diffusion and membrane selectivities

The effectivity of separation processes can be expressed by the selectivities. They are defined by the following formulas

$$\alpha_{ij}^{adsorption} = [N_j/N_i]_{adsorbed}/[[N_j/N_i]_{gas}$$

$$\alpha_{ij}^{diffusion} = D_j^{diffusion}/D_i^{diffusion}$$

$$\alpha_{i\,j}^{membrane} = \alpha_{ij}^{adsorption} \times \alpha_{ij}^{diffusion}$$

In these formulas N_i, and N_j denote the total particle numbers of kind *i* and *j* in the gas phase and in the adsorbed phase, respectively. Their ratio is also the ratio of the concentrations. D_i and D_j are the self-diffusion coefficients of kind *i* and *j*. The membrane selectivity is formed as the product of the adsorption selectivity and the diffusion selectivity.

Table 2 shows the different selectivities as obtained from the simulations. The selectivities have been calculated with the numbers of adsorbed particles from the GEMC simulations. The pressure is the equilibrium pressure of the GEMC simulations. It has been calculated from the densities that result from the simulations by the Peng-Robinson equation of state. The pressures are around 12 bar but somewhat different. The reason is that the resulting equilibrium pressure of a simulation cannot be predicted at the beginning of a simulation. It could have been adjusted by trial and error in additional simulations, but we believe that the results are clear enough also in this way.

From the results of Table 2 we can predict that MIL-127(Fe) is well suited to separate CO_2 from CO. As expected, the separation is more effective at lower temperature. The adsorption selectivity is somewhat larger than the membrane selectivity.

4. Conclusions

Adsorption and diffusion of an equimolar CO_2/CO mixture in MIL-127(Fe) was examined by molecular simulations at three different temperatures. Interestingly the adsorption of CO did not much depend on the temperature, while that of CO_2 showed quite large temperature dependence. This might be connected to the occupation of the most attractive adsorption sites by CO_2 molecules.

The most important adsorption sites in MIL-127(Fe) are the O_D and C_N atoms (explanations of the names can be found in the Fig. 2 of the lattice. Also the C atoms of adsorbed CO_2 molecules are quite attractive for other guest molecules CO_2 and CO.

Finally, it can be concluded that MIL-127(Fe) is well suited to separate CO_2 from CO, especially at lower temperature. The adsorption selectivity is somewhat larger than the membrane selectivity.

Combined pressure swing adsorption and temperature swing adsorption can be used to separate CO_2 from CO. Favourable would be adsorption from the mixture at low temperature and high pressure and desorption at high temperature and low (*e.g.* ambient) pressure.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.cplett.2018.02.032.

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Investigating adsorption- and diffusion selectivity of CO_2 and CH_4 from air on zeolitic imidazolate Framework-78 using molecular simulations

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ABSTRACT

The adsorption and diffusion of N_2, O_2 representing air, in ternary mixtures with CO_2 or CH_4, on Zeolitic Imidazolate Framework-78 are investigated by Gibbs ensemble Monte Carlo (GEMC) simulations for adsorption and by molecular dynamics (MD) simulations for diffusion. The adsorption and diffusion data are used for determining the membrane selectivities. N_2/O_2 ratios are found to be nearly the same in the gas and the adsorbed phase. At 228 K and low concentrations the CO_2/N_2 adsorption selectivity is found to attain values of as large as 140, further increasing with decreasing CO_2 concentration.

1. Introduction

Adsorption is one of the methods to separate mixtures or contaminations in raw materials (see Schüth et al. [1]). Even at low concentration, contamination with CO_2 can disturb processes, damage devices or reduce the quality of the products (see Hahn et al. [2], Boot-Handford et al. [3]). The separation of CO_2 or CH_4 from air counteracts the greenhouse effect (see Smit et al. [4]) and, by recovering CH_4, helps to reduce the usage of fossil fuels (see Chen et al. [5]). To date, there are many materials used to separate CO_2 and CH_4 from gas mixtures (Sumida et al. [6]), including polymer membranes (Lu et al. [7]), zeolites and metal organic frameworks (MOFs) (see Krishna and van Baten [8], He et al. [9], Li et al. [10], Sneddon et al. [11], Mihaylov et al. [12,13]), among them notably the zeolitic imidazolate frameworks (ZIFs) (Wang et al. [14], Diestel et al. [15]). ZIFs have high thermal and chemical stability (Park et al. [16]) and offer a large variety of different structures.

Thus, ZIFs are new promising candidates for this application. Particularly, the relatively high CO_2 capture of ZIF-78 and its excellent selectivity for CO_2/N_2 mixtures have been referred to in the literature (Banerjee et al. [17], Phan et al. [18], Li et al. [19], Park et al. [20], Sneddon et al. [11], Adatoz and Keskin [21]). But, investigations of the ternary mixture $CO_2/N_2/O_2$ corresponding to polluted air are still missing. Also the influence of the temperature over a larger range of temperatures has, to the best of our knowledge, not yet been investigated in detail. This is particularly interesting with respect to possible temperature swing procedures for removing CO_2 from air.

Atomic and molecular simulations have proven to be of large value for rationalizing a given material, *i.e.* for tracing the origin of its adsorption, diffusion and separation properties (see *e.g.* Keil et al. [22], Benzal et al. [23], Kärger et al. [24], Krishna [25], Zimmermann et al. [26], Titze et al. [27]).

This is of particular importance in cases where, as in the given case with ZIF-78, the host system has been found to offer particularly promising prospects for application in separation, including their relevance for the design of new ZIFs with even better properties. At present, many molecular simulation studies have been carried out on the adsorption and diffusion behavior in ZIFs, yielding very important data facilitating the in-depth understanding of their separation properties.

Recently papers have been published in which larger numbers of MOFs have been scanned within one publication to compare their usefulness for a given purpose (see Haldoupis et al. [28], Colon and Snurr [29], Li et al. [30], Erucar and Keskin [31]). *E. g.* in the paper Haldoupis et al. [28] more than 500 MOFs and more than 160 silica zeolites are considered. In Witman et al. [32] a family of 1-D rod topology sructures of MOF-74-type analogs are investigated and their CO_2 capture potential is examined.

Such high throughput studies seem to be the only way to keep an

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overview over the thousands of existing and the practically infinit number of possible MOF structures suitable for practical purposes. While this is, without doubt, a strategy of merit that gives valuable hints to experimentators and to industrial engineering it also has its shortcomings. Firstly, such simulations can be done only with rigid lattice because of the huge computational effort. In Hertäg et al. [33] it was shown that the use of a rigid lattice for the MD simulations overestimates the membrane selectivity for CH_4/H_2 separation in ZIF-8 by six orders of magnitude. The flexibility of the lattice is of particular importance if the kinetic diameter of the diffusing molecules is larger or, of the same size as the diameter of channels or windows that connect adjacent cavities. It is even more important in cases where the loading with guest molecules causes deformations of the lattice, like 'gate opening' (see Chokbunpiam et al. [34–36] and literature cited there). Secondly, interaction parameters between given sorts of lattice atoms with guest molecules that proved to work well for one MOF sometimes fail to work well for another one. Using parameters even proven to work sucessfully for some MOFs can lead to very different adsorption isotherms for another MOF (see tests in the results section of this paper). In papers scanning many MOFs for a given purpose usually one force field or two force fields are used for many MOFs. Thus, careful examinations for each single MOF if a flexible lattice is needed for given guest molecules and interaction parameters that have been checked by comparison with experiments for the special MOF under consideration still seem to be indispensible if more than an estimation is wanted.

For example in ZIF-8 the diameter of the rigid window is 3.4 Å (see Hertäg et al. [33], Chokbunpiam et al. [34–37]) and in ZIF-90 it is 3.5 Å (see Phuong et al. [38], Chokbunpiam et al. [39]). The kinetic diameter of methane is 3.8 Å (see Ismail et al. [40], Hertäg et al. [33]). Thus simulations of diffusion of methane in these two MOFs must be done with flexible lattice (for an ab initio treatment of this problem see Haldoupis et al. [41]). In ZIF-78 the window diameter is 4.4 Å (see Phan et al. [18]). The kinetic diameter of O_2 3.46 Å (see Ismail et al. [40]), that of N_2 is 3.64 Å Ismail et al. [40], Chokbunpiam et al. [36] and, that of CO_2 3.3 Å (see Ismail et al. [40], Chokbunpiam et al. [36]). Since the diameter of the windows of ZIF-78 exceeds that of the guest molecules considered in this paper by 0.6–1.1 Å the flexibility will have moderate influence on the diffusion of these species. Moreover, the flexibility will moderately enhance the diffusivity of all molecules. Thus the selectivity will be less affected than the self-diffusion coefficients themselves.

Banerjee et al. [17] investigated pore size control and functionality in isoreticular zeolitic imidazolate frameworks and their carbon dioxide selective capture properties. Adsorption isotherms of pure substances at 273 K, 283 K and 298 K have been measured separately. Their initial slopes have been used for determining adsorption selectivities for binary mixtures CO_2/N_2 and CO_2/O_2 at 298 K. It remains to check, whether these selectivities can be really found in mixture investigations. Moreover, it remains to investigate the temperature dependence over a larger range of temperatures. Both will be done in the present paper for the ternary mixtures of CO_2 and CH_4 with air, *i. e.* with the corresponding binary N_2/O_2 mixtures.

Phan et al. [18] compiled synthesis and structure data as well as carbon dioxide capture properties of zeolitic imidazolate frameworks. Among different ZIFs that have been compared in Table 2 of that paper ZIF-78 has the highest CO_2 uptake capacity (of 60.2 cm^3/cm^3) and the highest CO_2/N_2 selectivity (of 50.1) measured at 273 K.

Table 1
Structural properties of ZIF-78.

cell [Å]	angles [degr.]	ρ [g/cm^{-3}]	area [m^2/g]	cage size [Å]	aperture [Å]
a = 26.1147	α = 90	1.198	620	7.1	3.8
b = 26.1147	β = 90				
c = 19.4910	γ = 120				

Table 2
Lennard-Jones parameters and charges of the lattice atoms.

atom/molecule	σ [Å]	ε [kJ/mol]	charge in e
C_H1	3.43	0.3348	−0.2370
C_H2	3.43	0.3348	0.1520
C_H3	3.43	0.3348	−0.3213
C_N2	3.43	0.3348	0.1907
C_N3	3.43	0.3348	0.2242
C_N	3.43	0.3348	0.1482
O	3.12	0.1808	−0.4928
N_O	3.26	0.1889	0.7622
N	3.26	0.1889	−0.2420
H1	2.57	0.1176	0.1988
H2	2.57	0.1176	0.0862
H3	2.57	0.1176	0.2087
Zn	2.46	0.4440	0.8467

We used the Lennard Jones parameters for the lattice atoms from Liu and Smit [42]. These parameters have been tested successfully in Liu and Smit [42] for ZIF-68 and ZIF-69.

Sneddon et al. [11] compared different zeolite and MOF materials with respect to their use for CO_2 capture. It turns out that in a vacuum swing adsorption process ZIF-78 reaches the best sorbent selection parameter for the CO_2/N_2 separation at 298 K among all sorbents investigated.

In Liu and Smit [42] mixtures of CO_2/N_2 and CO_2/CH_4 and CH_4/N_2 on ZIF-68 and ZIF-69 were examined by Grand Canonical Monte Carlo (GCMC) simulations. The electrostatic interactions turned out to be a key factor in the selectivity. Also the influence of an additional small amount of water has been checked. However, for water contents of less than 5%, as considered in these two (ternary adsorption) systems, the influence of the water molecules was found to be negligibly small. In Li et al. [30] the adsorption of ternary mixtures of CO_2, N_2 and H_2O have been investigated in many MOFs in order to find out in which MOFs the unwished effect of the water has the lowest influence on the CO_2 capture.

In Li et al. [19] the adsorption of CO_2, N_2 and CH_2 and of the mixtures CO_2/N_2 and CO_2/CH_4 on ZIF-78 was also examined by GCMC simulations at 298 K. Selectivities are given as a function of the fugacity. The adsorption selectivity has been found to depend upon the molecular fractions of the adsorbed species. Interestingly, they also show that the selectivity is notably reduced by switching off the electrostatic interactions. MD simulations are not reported in this paper.

In all of these selectivity studies air was represented by N_2. Polluted air, however, consists of at least N_2, O_2 and the pollution. Hence, it seems to be desirable that the simulation of air cleaning includes O_2 as well. We are not aware of any such investigations with ternary mixture of CO_2, N_2, O_2 on ZIF-78 and therefore our studies are extended to this mixture.

According to Keil [43] the probability of adsorption for a molecule at an empty surface $S(0)$ is

$$S(0) = s_0 \exp\left\{\frac{-E_{ads}}{k_B T}\right\}. \tag{1}$$

s_0 is a constant prefactor and E_{ads} is the adsorption energy (which has negative values, if adsorption takes place). Let us consider two types of molecules 1 and 2 with different adsorption energies. *E.g.* 1 means CO_2 and 2 means N_2 and $|E_{ads,1}| > |E_{ads,2}|$.

$$\frac{S_1(0)}{S_2(0)} = \frac{s_{0,1}}{s_{0,2}} \exp\left\{\frac{-(E_{ads,1} - E_{ads,2})}{k_B T}\right\} = \frac{s_{0,1}}{s_{0,2}} \exp\left\{\frac{|E_{ads,1} - E_{ads,2}|}{k_B T}\right\}. \tag{2}$$

Thus, the selectivity at infinite dilution should increase with decreasing temperature as an exponential function of $1/T$. Therefore, we extended the study to lower but, techically feasible temperatures.

We have based our investigations of membrane selectivities on the combined application of Gibbs ensemble Monte Carlo (GEMC) and molecular dynamics (MD) simulations via the calculation of adsorption- and diffusion selectivities. As a matter of course, meaningful calculations of both selectivities have to be performed for identical temperatures and guest concentrations. One is thus confronted with the problem that, on calculating diffusion selectivities via MD, one has to do with only a very small number of adsorbed CH_4, N_2, O_2 molecules giving rise to bad statistics.

To overcome this problem very long runs and large systems have to be used. But, long runs with large systems can hardly be performed with flexible lattice.

Consideration of lattice flexibility, however, is known to be crucial for a correct determination of diffusivities of molecules like CH_4 in some ZIFs (Hertäg et al. [33], Haldoupis et al. [41]). Hence, before performing MD in a rigid lattice the importance of the flexibility has to be discussed for the case examined here.

In contrast, it is well known that for the Monte Carlo simulations of adsorption the flexibility of the lattice is of minor importance because the frequency of occurrence of window passages influences only the speed of approach to the adsorption equilibrium rather than the adsorption equilibrium itself. Of course, passages must be at least possible for adsorption and the adsorbed species must not change the structure of the ZIF. If these two conditions would not be fullfilled then simulations with rigid lattice would not be a good approximation, even for adsorption. All Monte Carlo simulations (MC) of adsorption equilibria in the literature have been found to be done with a rigid lattice. This approximation has also been checked and confirmed in several papers (see Zhang et al. [44], Phuong et al. [38]). The advantage of MC in comparison to MD for static equilibria consists in larger changes per simulation step thus leading to better statistics with less effort. This advantage would be lost in MC with flexible lattice.

2. Computational details

ZIF-78 is composed of zinc tetrahedral clusters linked by 2-nitroimidazole (nIM) and 5-nitrobenzimidazole (nbIM) (Fig. 1). The structural properties of ZIF-78 are characterized by the data given in Table 1.

Fig. 1 shows the structure and the unit cell of ZIF-78.

According to their positions and chemical bonds atoms even of the same sort can have different interaction parameters. Therefore, different atom sorts have been defined that are explained in Fig. 2. Note, that CH_1 does not mean that this C is connected with an H1 atom. Instead, it is the first one of the CH atoms and its properties depend upon their complete environment, not only upon the connected H atom.

In all of our simulations we use periodical boundary conditions. In spite of the non-rectangular shape of the unit cell, following the ideas of Leyssale et al. [45] and Sant et al. [46] we can cut a rectangular basic cell from the infinite lattice as explained in the supporting material. Note, that because of $\gamma = 120$ degree and $\cos(\pi - \gamma) = 0.5$ a pair number of unit cells in z-direction have to be included before cut in order to obtain full periodicity. For details see the supporting material.

The rectangular cell that contains the atoms of 4x4x4 unit cells has the dimensions 104.4696 x 90.4733 × 77.9640 $Å^3$. In smaller simulation cells the statistics was too bad to obtain self-diffusion coefficients from the MD simulations with acceptable accuracy.

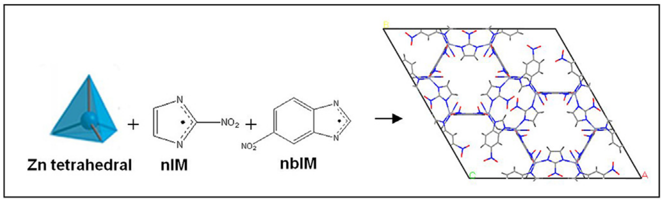

Fig. 1. Crystal structure of ZIF-78.

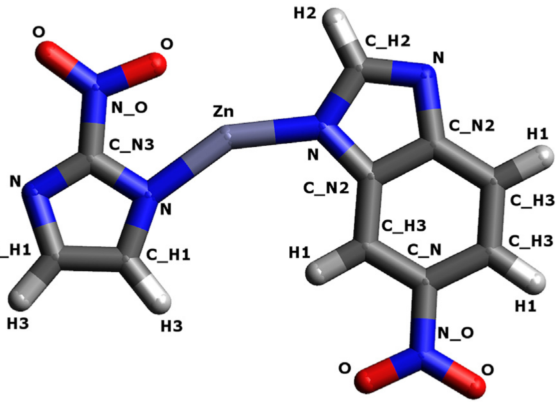

Fig. 2. Atom types in the lattice of ZIF-78.

The LJ parameters for the interaction of atoms of different types (σ_{ij} and ε_{ij}) are obtained from that for pure types (σ_{ii} and ε_{ii}) by the rules of Lorentz-Berthelot

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \qquad \varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}. \tag{3}$$

The Lennard-Jones parameters and charges of the lattice atoms are given in Table 2.

All partial charges of the lattice atoms were extracted by quantum calculation using the Gaussian 09 program package calculating the partial charges of ZIF-78, using the HF/6-31 + G(d) theory and the electrostatic potential fitting (ESP) of Merz-Singh-Kollman (MK) Singh and Kollman [47], Besler et al. [48].

Different force fields are reported in the literature that worked well for CH_4, CO_2, N_2 and O_2 guest molecules within some porous solids. Unfortunately there is no general force field among them that would also work for the adsorption of these substances in ZIF-78.

The Lennard-Jones parameters and partial charges of oxygen and nitrogen have been taken from Yang et al. [49]. Both are modeled as dumbells and an additional fictive charge center is introduced at the middle of the bond in both cases. The N-N bond length is 1.1 Å and the O-O bond length is 1.21 Å. The LJ parameters and charges are given in Table 3 where x means the fictive charge center. In order to check all the parameters we have calculated adsorption isotherms of the pure substances at 298 K by Gibbs Ensemble Monte Carlo (GEMC) and compared the results with experiments. The curves are given and discussed in the results section.

For CH_4 we used a united atom model. The very small acentric factor of 0.01 of the CH_4 molecule (see Reid et al. [50]) supports a spherial approximation like *e.g.* also in Liu and Smit [42].

We have compared adsorption isotherms for CH_4 using parameters from several papers in ZIF-78 with the experimental values of Banerjee et al. [17]. Unfortunately, well established generalized potential parameters that can be used for any ZIF, do not exist. Hence, we are forced to find another value for the ε of CH_4 in ZIF-78 in order to reproduce the adsorption of CH_4 in agreement with the experimental values of

Table 3
Lennard-Jones parameters and partial charges that are used for the atoms in guest molecules and the united atom guest molecule CH_4 in this paper.

atom/molecule	σ [Å]	ε [kJ/mol]	charge in e
N in N_2	3.31	0.2993	−0.4820
x in N_2	0	0	0.9640
O in O_2	3.02	0.4074	−0.1130
x in O_2	0	0	0.2260
C in CO_2	3.43	0.4393	0.7
O in CO_2	3.12	0.2510	−0.35
CH_4	3.73	1.3968	0

Banerjee et al. [17]. Since no one of the parameter sets from the literature could reproduce the CH_4 adsorption in ZIF-78 satisfactorily we had to find own parameters that yielded good agreement with Banerjee et al. [17] as can be seen in the results section. It has been assumed that the thus confirmed potential can be used to examine also other properties of the system, like structure of the adsorbed gases, mixture adsorption, diffusion and selectivities well.

All LJ parameters for the guest molecules that are used in this paper can be found in Table 3.

The GEMC technique Panagiotopoulos [51,52], Theodorou [53] is described in the supporting material. Its basic idea is the simultaneous simulation of the mixture in the gas phase (in box A) and adsorbed phases within the ZIF (in box B). Equilibrium of gas and adsorbed phases with each other is maintained by particle exchange fulfilling the condition of microscopic reversibility. The pressure can be obtained in the gas phase in order to avoid problems that occur when the pressure within a porous solid loaded with charged guest molecules is evaluated. For pressures up to 1–2 bar the ideal gas equation of state is a good approximation as explained in the supporting material. Hence, the pressure in the gas phase (box A) for the equilibrium state can easily be calculated. The simulation then yields the amount of guest molecules, in equilibrium with the gas box.

A comparison of the adsorption isotherms obtained from the GEMC simulations with measurements for different pure substances is given in Fig. 3 and in Fig. 4 in the results section. It is seen to justify our choice of the parameters.

The pressure is adjusted by varying the gas box size while the size of the ZIF simulation box remains unchanged.

As the adsorption equilibrium is not known in advance, the appropriate numbers of CH_4 or CO_2 and the proper gas box size have to be found by trial and error in test runs. Fortunately, the ratio O_2/N_2 in the gaseous phase (feed) is not much disturbed by the adsorption processes considered in this work and turned out to be very close to the value of 26.8% for all runs. Hence, no adjustment of this ratio is needed. A test of the influence of small perturbations of this ratio on the CO_2/N_2 selectivity at low temperature, where this perturbation has the largest value, is given in the results section.

During each GEMC run the total number of molecules of each type is conserved. The simulation yields their amounts in the adsorbed and gaseous phases.

The system contains 2696 N_2 and 722 O_2 molecules in each GEMC simulation run. In order to find the total amount adsorbed as a function of the pressure at constant temperature and constant concentration ratio and as a function of the concentration ratio at constant pressure and temperature the total number of CO_2 (or CH_4) molecules and the size of the gas box have to be adjusted for each data point.

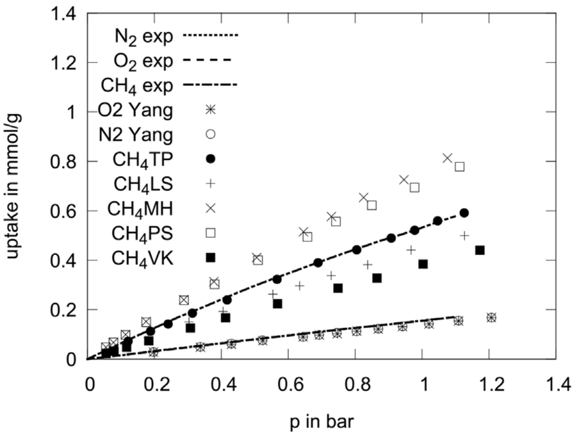

Fig. 3. Adsorption isotherms for single component adsorption of CH_4, N_2, O_2 in ZIF-78 obtained from GEMC using different force fields compared with the experimental results from Banerjee et al. [17].

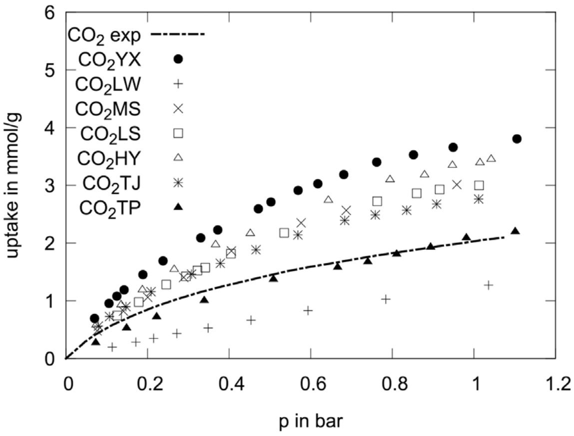

Fig. 4. Adsorption isotherms for single component adsorption of CO_2 in ZIF-78 obtained from GEMC using different force fields.

For the adsorption isotherms the CO_2/N_2 or CH_4/N_2 ratio is kept constant at the value 0.1 in the feed (gas phase) in equilibrium. For the investigation of the concentration dependence of the adsorption selectivity the pressure has been kept constant at 1 bar.

The content of CO_2 or CH_4 of 10% of the N_2 content is higher than that in air under normal conditions and corresponds to industrial waste or smoke. Very small content of pollution cannot be simulated because of bad statistics for small particle numbers.

By periodical boundary conditions a quasi infinite system is simulated and boundary effects are avoided.

It turned out that the fluctuations in the amount adsorbed of CO_2 have been very big and could persist for many millions of simulation steps. Thus, for CO_2 at 228 K we needed up to more than ten continuation runs, each of 20 million steps in order to find reliable values for the uptake. In contrary, for CH_4 20 million steps of equilibration and subsequently 20 millions steps for evaluation have been found to be sufficient in almost all cases.

The criteria for the reliability are relatively small fluctuations around a stable value and agreement of the chemical potentials for each type of molecules in gas phase and adsorbed phase.

The ZIF-78 simulation box contains 41,472 lattice atoms (corresponding to 4 × 4 × 4 = 64 unit cells). Periodical boundary conditions are also applied to this lattice.

The GEMC simulations have been performed with rigid ZIF-78 lattice. Monte Carlo simulations, like Grand Canonical Monte Carlo (GCMC) or GEMC, with flexible lattice would not make sense because the main advantage of MC over MD would be lost. This advantage consists in the size of the random changes per simulation step in MC that are orders of magnitude larger than the displacements per time step in MD. Thus, statistically independent situations are created by MC much more effectively. On the other hand, dynamical properties like diffusion must be examined by MD because a time scale is missing in MC.

After typically 60–200 millions of simulation steps, depending upon pressure and temperature, equilibrium between box A and box B will be reached for the CO_2 air mixture and the final equilibrium will be studied during additional 20 millions of steps.

An adsorption selectivity $\alpha_{A,\mu,\nu}$ may be defined using the formula van de Graaf et al. [54], Krishna and van Baten [55] for a binary mixture of molecules of types μ and ν

$$\alpha_{A,\mu,\nu} = \frac{N_{\mu,ads}/N_{\nu,ads}}{N_{\mu,gas}/N_{\nu,gas}}, \tag{4}$$

where $N_{\mu,ads}$ is the number of adsorbed molecules of type μ in the ZIF (box B) and $N_{\mu,gas}$ is the number of molecules of type μ in the gas phase (box A) *etc.*. Correspondingly, this definition has also been applied to 2 of 3 types of molecules in a ternary mixture.

Moreover, molecular dynamics simulations (MD) (see Allen and Tildesley [56]) have been carried out for the molecules that are adsorbed in the ZIF at 1 bar in order to find the diffusion selectivity of the above mentioned molecule types μ and ν

$$\alpha_{D_s,\mu,\nu} = \frac{D_{s,\mu}}{D_{s,\nu}}. \tag{5}$$

The self-diffusion coefficients of the guest molecules were determined from the linear fits to the computed mean square displacements (MSDs) of the molecules. The MSD of molecules of type ν is defined by

$$MSD_\nu(t) = \left\langle \frac{1}{N_\nu} \sum_{i=1}^{N_\nu} [\vec{r_i}(t_0) - \vec{r_i}(t_0 - t)]^2 \right\rangle_{t_0} \tag{6}$$

where the $\vec{r_i}(t)$ is the position of molecule i and the average $<...>_{t_0}$ is carried out over many different time origins t_0. N_ν is the number of molecules of type ν. The self-diffusion coeffcient D_s has been determined from the best linear fit of the relation

$$MSD_\nu(t) = 6 \cdot D_{s,\nu} \cdot t + \beta. \tag{7}$$

β is a fitting parameter that takes into account that for very short times the movement of the molecule is a ballistic flight rather than an irregular thermal motion.

The numbers of molecules in our MD simulation that have been chosen according to the uptake results at 1 bar are very small, requiring long simulation runs in large systems except for CO_2. For example at 298 K, even in a large simulation box of 4x4x4 unit cells, there are only 17 O_2 molecules adsorbed in the CO_2/air mixture and 19 O_2 molecules adsorbed in the CH_4/air mixture. For such small particle numbers very long simulation runs are necessary in order to obtain a reliable diffusion coefficient. But, the MD simulation box of 4x4x4 unit cells is too big for long runs with flexible lattice.

Taking into account the reflections about guest molecule sizes and window sizes in ZIF-78 in the introduction, the increase of the D_s by lattice flexibility values is expected to be moderate for N_2, O_2, CO_2 and CH_4 and that this increase will even partially be cancelled if D_s values are divided by each other. The diffusion selectivities may thus, in first-order approximation, be assumed to be the same in flexible and rigid lattice. Hence, we carried out the MD simulation in a rigid box of 4x4x4 unit cells.

We learned from the GEMC simulations that fluctuations in this system have a very long lifetime. Each MD simulation run has been started therefore with a 20 ns long equilibration run before starting the evaluations. The simulation time step was 0.005 ps. After equilibration, trajectories of 20 ns have been calculated from which the MSDs have been obtained.

3. Results and discussion

3.1. Adsorption results

3.1.1. Parameter verification by simulated adsorption isotherms

Fig. 3 shows a comparison of adsorption isotherms for CH_4, N_2, O_2 in ZIF-78 obtained from GEMC using different force fields compared with the experimental results from Banerjee et al. [17]. As mentioned above the parameters for N_2 and O_2 have been taken from Yang et al. [49]. They yield good agreement with the experiment of Banerjee et al. [17].

But, for CH_4 and CO_2 we could only find parameter sets that did not lead to an agreement with results of Banerjee et al. [17]. First we have compared isotherms from different parameter sets for CH_4. LS means that parameters from Liu and Smit [42] have been used. MH belongs to the parameters of Mendoza-Cortes et al. [57]. PS means the parameters taken from Prakash et al. [58]. VK means the TraPPE force field of Martin and Siepmann [59] that was also used in Vlugt et al. [60], Hertäg et al. [33]. Since no one of these parameter sets could be used to reproduce the experiment we had to modify one of them. TP means 'this paper'. We have chosen the widely accepted LJ diameter 3.73 Å of the TraPPE force field of Martin and Siepmann [59]. Tests with different values of ε finally led to the best result for $\varepsilon/k_B = 166$ K.

Fig. 4 shows a comparison of adsorption isotherms for CO_2 adsorption in ZIF-78 obtained from GEMC using different force fields with the experimental adsorption isotherm given in Banerjee et al. [17]. This isotherm has been measured only for the interval between 0 and about 1 bar.

In all of the models compared here, CO_2 is modeled by a linear triatomic molecule with three LJ interaction sites. Point charges are located at these three LJ interaction sites to reproduce the quadrupol moment of CO_2.

Model YX uses the TraPPE force field of Jeffrey et al. [61] for CO_2. The charges have been fitted to reproduce the vapor-liquid phase diagram of the binary mixture of CO_2/propane. These parameters have also been used in Yang et al. [49], Walton et al. [62]. The LW results have been obtained using parameters from Liu et al. [63] that is based on the LJ parameters of the UFF force field Rappe et al. [64]. The charges have been fitted to meet the first-order electrostatic and second-order conduction interaction. In Evanseck et al. [65] a parameter set is proposed that is named TJDM1 and compared with parameters that are reported to be derived from data given in Murthy et al. [66]. In Murthy et al. [66] the quadrupol moment is given but, no point charges. Hence, in Evanseck et al. [65] the point charges must have been fitted to meet the quadrupole moment of Murthy et al. [66]. These two parameter sets have been used in our curves TJ and MS, respectively. The LS model uses parameters from Liu and Smit [42]. These parameters are similar to that of the MS model. HY corresponds to parameters from Harris and Yung [67] that have also been used in the paper of Zheng et al. [68].

Since no one of these isotherms agreed with the experiment for ZIF-78, we had to modify these parameters in this paper. In all of the mentioned papers the LJ parameters and the partial charges have been found by separate methods. Hence, it should be possible to combine them in different ways. We found after many trials that a combination of the UFF LJ parameters of Liu et al. [63] and the charges of Yang et al. [49] gave good agreement with the experiment for the CO_2 adsorption and we used it in the present paper. TP means this paper.

The adsorption isotherms at 298 K, named TP in Fig. 3 and in Fig. 4, for the pure substances N_2, O_2, CO_2 and CH_4 show good agreement with the experimental data reported in ref. Banerjee et al. [17]. Thus it is promising to use these parameters for the investigation of also structure, diffusion and mixture properties.

Most interestingly, for all pressures considered the ratio of the amounts of N_2 and O_2 are found to be almost equal in the adsorbed and gaseous phases. With these adsorption properties, air behaves as if it would be one component. But, this is a result of our research and could not be assumed in advance without prove.

3.1.2. CO_2 in air

Equilibria of O_2 and N_2 molecules, representing air and CO_2 as pollution have been investigated at $T = 228$ K, $T = 258$ K and $T = 298$ K. The pressure region for the adsorption isotherms was 0–4.5 bar. This is the most interesting region because CO_2 is strongly adsorbed already at low pressure. At higher pressures the slope of the adsorption isotherm for CO_2 becomes smaller and the increase of the O_2 and N_2 content will reduce the adsorption selectivity.

Since the adsorption isotherms for pure O_2 and N_2 widely agree, the question arises if the ratio O_2/N_2 in the gas phase is kept automatically close to the predefined value of 26.78% in all adsorption runs. This is, fortunately, the case.

Fig. 5 shows the ratio O_2/N_2 in the gas phase found in all of the GEMC simulations of the ternary $CO_2/O_2/N_2$ mixture at different

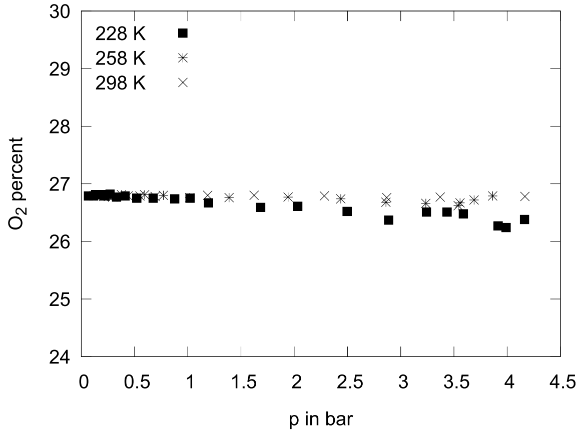

Fig. 5. The ratio O_2/N_2 in the gas phase found in the GEMC simulations of the ternary $CO_2/O_2/N_2$ mixture at different temperatures and pressures.

temperatures and pressures. Thus it needs no adjustment that would have required many additional trial and error runs since several parameters have to be adjusted simultaneously.

Note, that also the number of N_2 and O_2 in the gas phase in equilibrium is, of course, different for different pressures while the total numbers of 722 O_2 and 2696 N_2 molecules are always the same in all GEMC simulations of this work, except the following tests:

The goal of the investigation is to explore the CO_2/N_2 selectivity. To be sure that the remaining deviations of the O_2/N_2 ratio do not change the results for this selectivity, additional runs with different O_2/N_2 ratio have been undertaken at 4.1 bar, 228 K where the observed deviations (see Fig. 5) have quite large values. The O_2 content was modified within the ternary mixture with a CO_2/N_2 ratio of 0.1 in the gas phase.

Table 4 shows that even within a larger range than the observed one the influence of this percentage on the CO_2/N_2 selectivity is below the size of the fluctuations.

Thus it was sufficient to use the same total numbers of N_2 and O_2 molecules for all investigated pressures and temperatures and, to adjust the pressure and the number of CO_2 molecules. The pressure was changed by choosing the size of the gas box. Runs with different CO_2 numbers and different box sizes have to be done in any case for ensuring by trial and error that the number of CO_2 molecules amounts to 10% of the number of N_2 in equilibrium.

Fig. 6 shows the uptake of the three gases as a function of the pressure for three different temperatures. Note, that the pressure in Fig. 6 is the final equilibrium pressure of the equilibrium composition in the gas box.

In contrast to CO_2 the amount of adsorbed molecules of types N_2 and O_2 seems to be far from saturation, even in the mixture when CO_2 is filling some space in the cavities. Hence, the selectivity is expected to become smaller if the pressure is increased up to *e.g.* 6–10 bar which is the pressure usually used in technical pressure swing adsorption.

Fig. 7 shows the CO_2/N_2 adsorption selectivity in the ternary mixture $CO_2/N_2/O_2$ as a function of the pressure (left hand side). The concentration dependence of the selectivity at different temperatures and constant pressure of 1 bar can be seen on the right hand side of Fig. 7.

Table 4
Influence of small perturbations of the oxygen percentage in the feed on the CO_2/N_2 selectivity.

percent oxygen	CO_2/N_2 selectivity
24.73	96.174
25.26	94.329
26.38	94.149
27.26	95.851
28.12	98.945

The CO_2/N_2 adsorption selectivity in the ternary mixture at 228 K at low pressures reaches values of more than 140. It depends strongly upon temperature and pressure. The pressure dependence at higher temperatures is less pronounced.

For comparison with the literature we note that from Fig. 7 it can be seen that the selectivity at 298 K is approximately 30 for low pressure and about 25 for 1 bar. Banerjee et al. [17] estimated from the initial slopes of the isotherms of pure substances a value of 50 for the CO_2/N_2 selectivity which is higher than our value for this selectivity directly found in the ternary mixture. But Fig. 4 shows that the isotherm of CO_2 shows nonlinear behavior already at pressures as low as 0.2 bar and the slope of the isotherm becomes smaller with increasing pressure. Hence, conclusions from initial slopes to 0.2 bar and higher pressures should yield higher selectivities than found in reality. Moreover, the assumption of an ideal gas mixture that is implicitely contained in the use of the slopes of pure substances appears questionable.

Phan et al. [18] found in the binary mixture CO_2/N_2 a selectivity of 50.1 measured at 273 K in the low pressure region. The pressure is not given explicitely. But, this would be important because of the mentioned non-linearity which means that validity of Henry's law cannot be assumed. Only for linear adsorption isotherms the adsorption selectivity can be implied to be independent of pressure. Moreover, the CO_2/N_2 ratio in the gas phase is not mentioned. Nevertheless, taking into account that the selectivity at 273 K should be between our values for 253 K and 298 K, that we found for the 10% mixture, the agreement seems to be quite good.

Taking into account that the selectivity increases with decreasing temperatures this value is not so very different from our value in the ternary mixture. In Li et al. [19] GCMC results from different force fields at 298 K are compared. Their selectivities using the DREIDING force field are about 50 at very low pressure (they use fugacity instead of pressure) and for increasing pressure their selectivity decreases to about 35 for the binary mixture which agrees approximately with our results for the ternary mixture. Interestingly, they show that switching off the electrostatic interactions notably reduces the selectivity. This is no surprise and illustrates the important role of the large quadrupole moment of CO_2.

Interestingly, Fig. 7 shows that a decrease of the temperature increases the adsorption selectivity drastically. Therefore a temperature swing method for separation processes appears to be attractive. Because also a decrease of the pressure increases the selectivity, a simple decompression of the feed gas, that leads to both a lower temperature and pressure, might be a promising way towards selectivity enhancement.

As mentioned above, the concentration of CO_2 in air is normally much smaller then 10%. But, calculations with small numbers of CO_2 molecules require very long runs to get reasonable statistics. Hence, we decided to check the selectivities for lower loadings only at 1 bar. The increase of the selectivity with decrease of the CO_2 concentration makes ZIF-78 an interesting adsorbent for removing even small amounts of CO_2 from air where other methods have problems.

In our calculations of the isotherms (and, thus, of also adsorption selectivities) for the higher pressures (of up to 1.2 bar) fluctuations turned out to occur with very long durations, as mentioned in the technical details. As a consequence, calculations of more than 200 million steps were needed in some cases to get reliable values for uptakes and selectivities. For getting smoother curves, at least a 4–5 times larger computational effort would be necessary. We had therefore to confine ourselves to the presented simulations in which, however, the trends in selectivity as function of temperature and pressure become clearly visible.

3.1.3. CH_4 in air

Fig. 8 shows the O_2/N_2 ratio in the $CH_4/O_2/N_2$ mixture. In spite of the large pressure range and the different adsorbed amounts of all gas molecules, the O_2/N_2 ratio is quite insensitive against these influences.

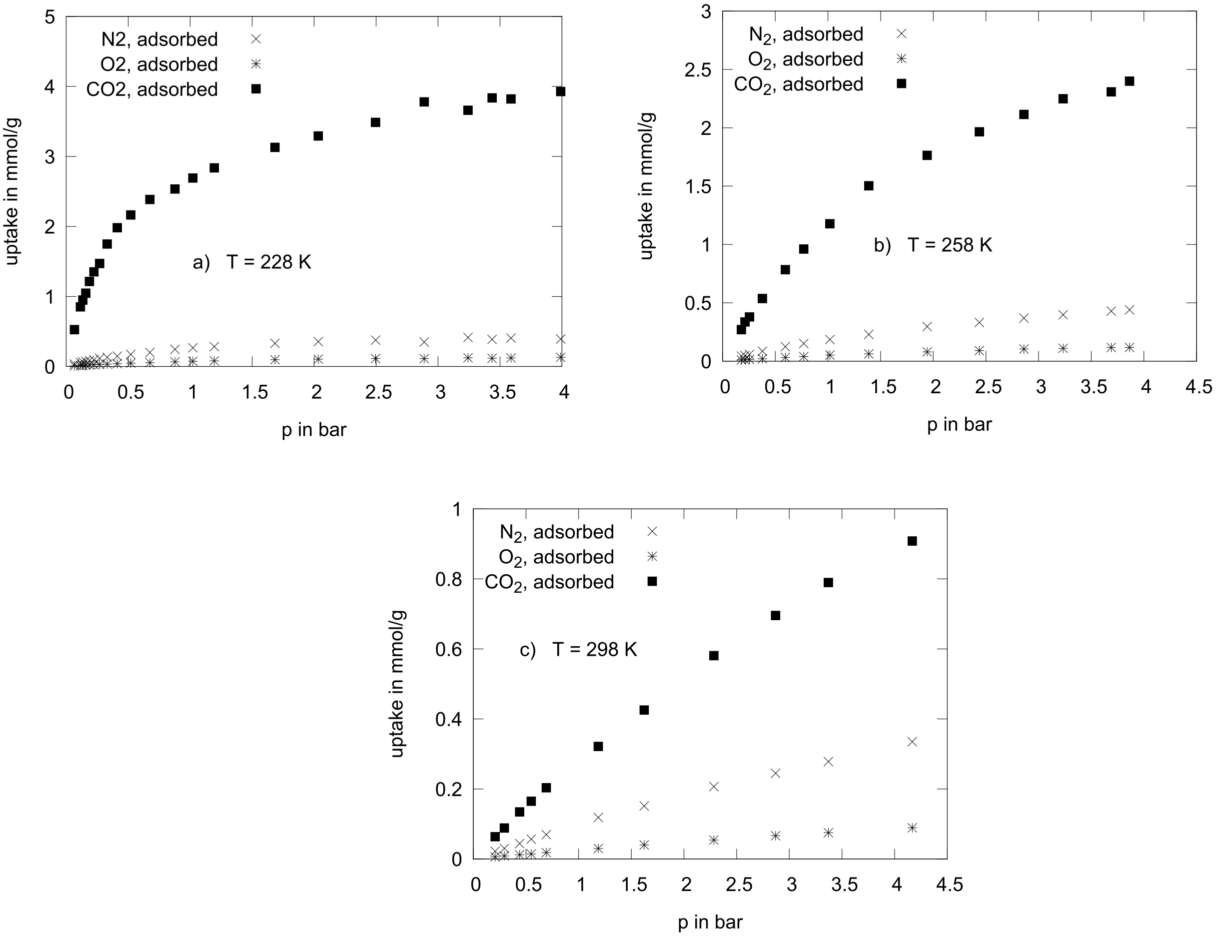

Fig. 6. Uptakes for the CO_2/air mixture (with O_2/N_2 as in Fig. 5 and $CO_2/N_2 = 0.1$ in the gas phase) in mmol/g as a function of the pressure at different temperatures.

In Fig. 9 the adsorption isotherms for a mixture CH_4/air are given. The preparation of the system and the technical details were the same as described in the case of CO_2.

Fig. 10 shows the adsorption selectivity for CH_4/N_2 in the ternary $CH_4/N_2/O_2$ mixture as defined in Eq. (4) as a function of the total pressure at different temperatures (left) for a ratio of 0.1 of CH_4 to N_2 molecules and of the concentration of CH_4 at 1 bar, also at different temperatures.

In contrary to CO_2 adsorption the concentration dependence of the CH_4/N_2 selectivity in air is quite small.

3.2. Radial distribution functions (RDFs)

The radial density functions (RDFs, see Allen and Tildesley [56], Leach [69]) have been exploited for visualizing structural properties of the adsorbed gases.

Fig. 11 shows the RDFs of the C atom of CO_2 and of the O atom of CO_2 determined in the present study with respect to the different lattice atoms, *e.g.* with O_L and N_L meaning the oxygen and carbon of the lattice in contrast to the O of CO_2 and of the nitrogen in the air. The temperature was $T = 228$ K and the total pressure was 1 bar. Moreover the potential energy of each CO_2 has been analyzed. The lowest potential

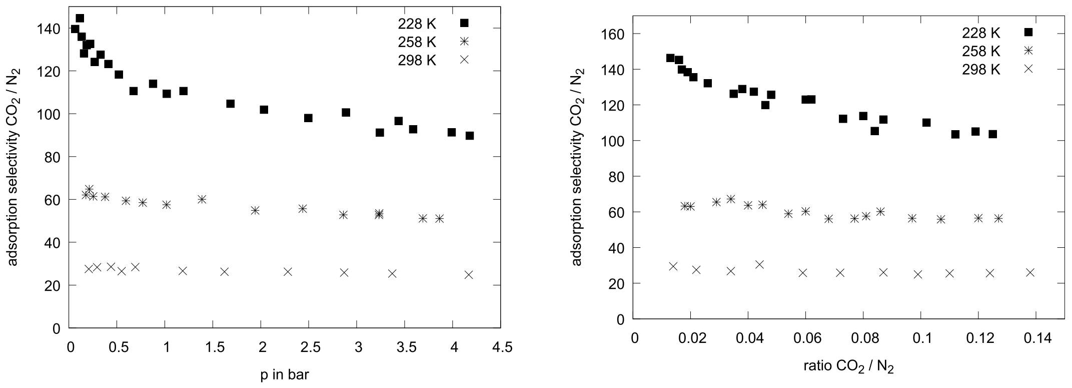

Fig. 7. Adsorption selectivity CO_2/N_2 as defined in Eq. (4) as a function of the pressure at different temperatures (left) for a ratio of 0.1 of CO_2 to N_2 molecules and of the concentration of CO_2 at 1 bar, also at different temperatures (right).

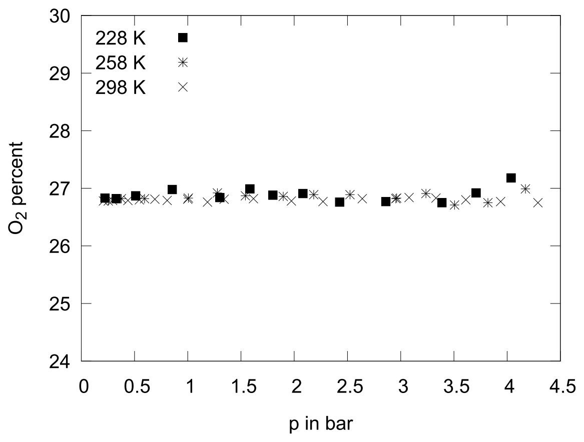

Fig. 8. The ratio O_2/N_2 in the gas phase found in the GEMC simulations of the ternary $CH_2/O_2/N_2$ mixture at different temperatures and pressures.

energy that an CO_2 molecule had during the whole simulation run was −34.54 kJ/mol. The closest lattice atom in the moment when this CO_2 molecule had this low potential energy was an lattice oxygen at a distance of 3.10 Å from the center of mass of the CO_2. This fits well to the first peaks of the C atom and of the O atom of CO_2 with the oxygen of the lattice. These peaks are the highest ones. Only that of CO_2 with Zn is comparable but at much larger distance. Thus, an adsorption site close to the oxygen atom of the lattice is indicated. This adsorption site and the low potential energy at this position nicely correspond with the large amount of CO_2 adsorbed and its small self-diffusion coefficient.

The high peak in the RDF with Zn is at a distance of about 6 Å. Hence, no adsorption site can be close to the Zn. Instead, the peak indicates the high probability to find a CO_2 with more than one Zn lattice atoms simultaneously at a distance of roughly 6 Å.

Energetic studies of the adsorption sites of CO_2 in ZIF-78 have been reported in Park et al. [20].

Fig. 12 shows the RDFs of CH_4 with different lattice atoms. Two first peaks can be seen. One is close to the lattice carbon C_H1 and one close to the lattice hydrogen H3 which is a neighbour of C_H1. Thus an adsorption site close to C_H1 is indicated by both of them.

The lowest potential energy of −22.66 kJ/mol has been found when a methane was close to a lattice carbon C_H1. The distance between the centers of mass was 3.09 Å in that moment.

Again there are higher peaks CH_4-Zn at distances of 5 and 6 Å that must be caused by the simultaneous presence of more than one Zn atom.

3.3. Self-diffusion coefficients (D_s) from MD and membrane selectivities

As described in Eq. (6) mean square displacements (MSDs) of the molecules are evaluated and self-diffusion coefficients (D_s) are obtained from the slope of linear fits of the MSDs. The D_s resulting from MD simulations in the rigid lattice of 4x4x4 unit cells of ZIF-78 are given in Table 5.

As pointed out in the computational details the small guest particle numbers make it difficult to calculate reliable self-diffusion coefficients (D_s) even in the big system of 4x4x4 unit cells (41,472 lattice atoms). Each long trajectory is just sufficient to calculate one D_s value and therefore error bars cannot be obtained. A tentative estimation basing

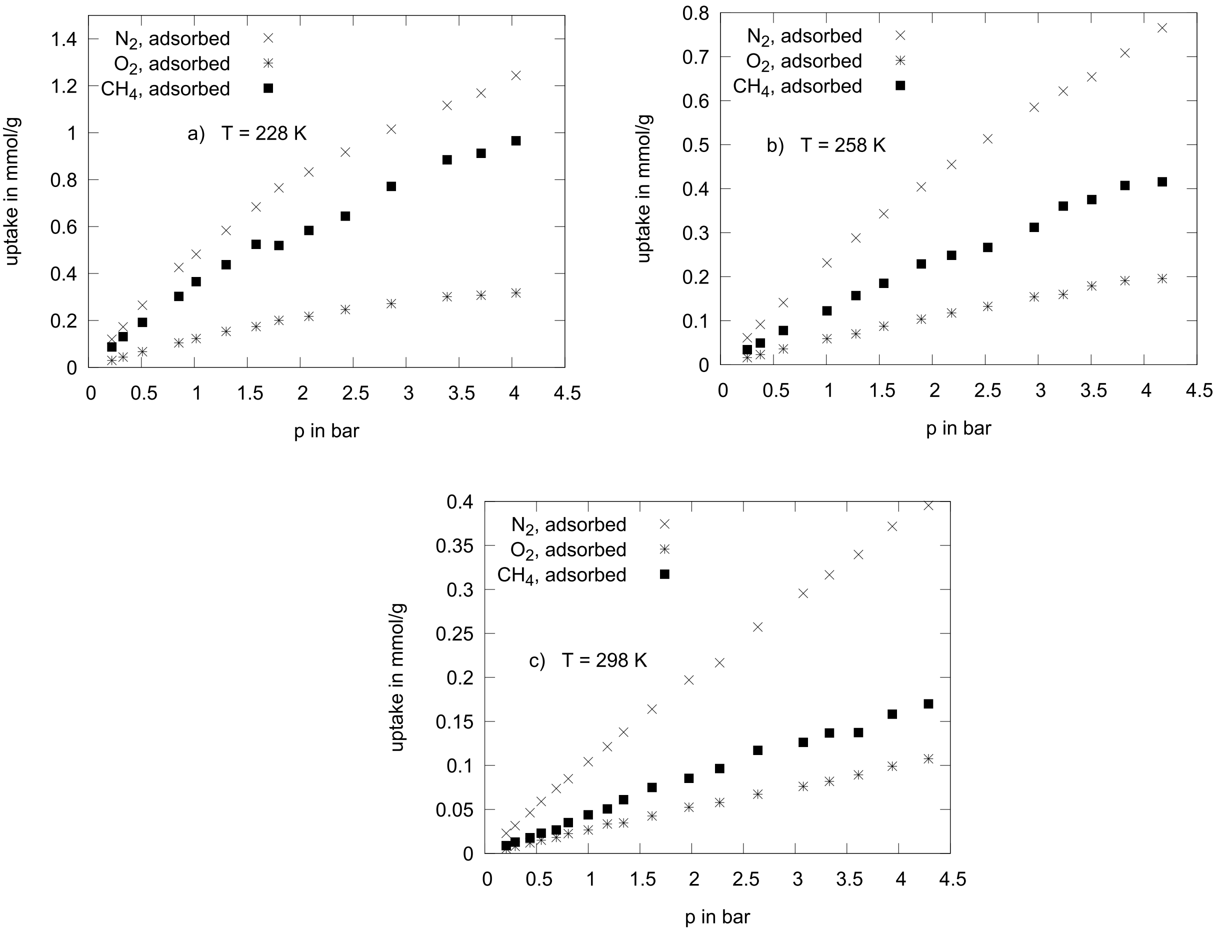

Fig. 9. Uptakes for the CH_4/air mixture (with O_2/N_2 as in Fig. 8 and CH_4/N_2 = 0.1 in the gas phase) in mmol/g as a function of the total pressure at different temperatures.

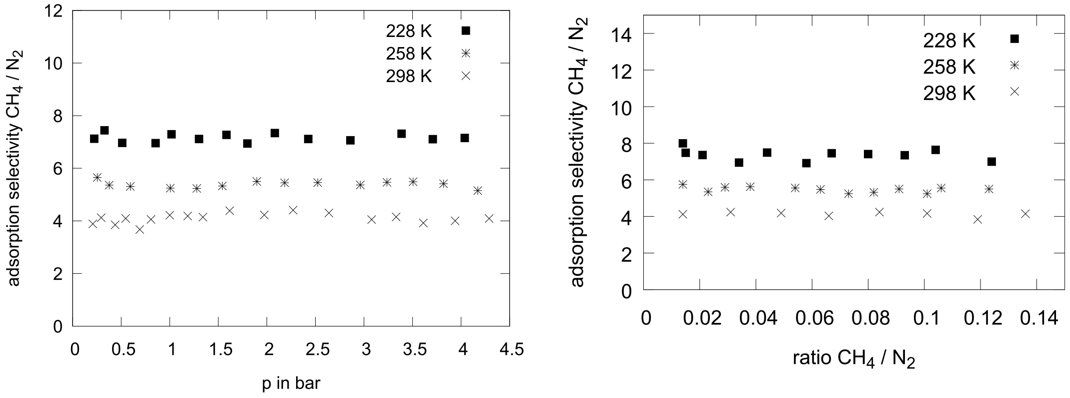

Fig. 10. Adsorption selectivity CH_4/N_2 as defined in Eq. (4) as a function of the pressure at different temperatures (left) for a ratio of 0.1 of CH_4 to N_2 molecules and of the concentration of CH_4 at 1 bar, also at different temperatures (right).

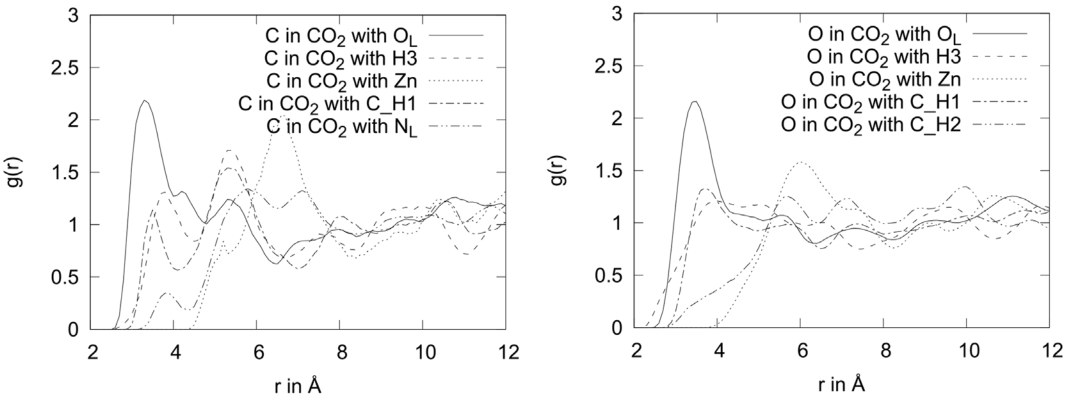

Fig. 11. RDFs of the C atom of CO_2 and of the O atom of CO_2 with the different lattice atoms. O_L, N_L mean the oxygen and nitrogen of the lattice. The temperature was $T = 228$ K and the total pressure was 1 bar.

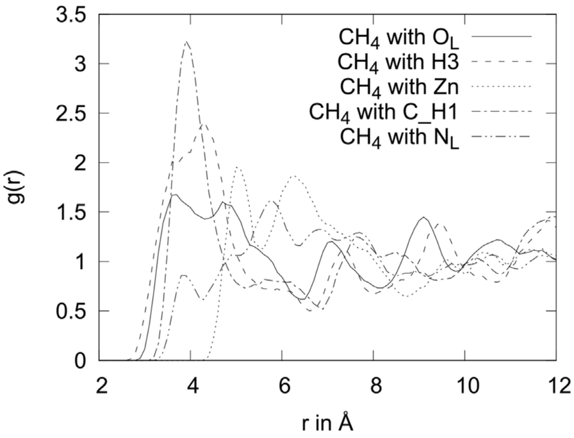

Fig. 12. RDFs of CH_4 with the different lattice atoms. O_L, N_L mean the oxygen and nitrogen of the lattice. The temperature was $T = 228$ K and the total pressure was 1 bar.

on the shape of the MSDs would be that the error can be about 20%.

Some examples for MSDs at 298 K are given in the supporting material.

Interestingly, the results in Table 5 show that although the self-diffusion coefficients of CH_4 and CO_2 are not very different in their corresponding mixtures, the self-diffusion coefficients of N_2 and O_2 are significantly smaller in the mixture with CO_2. This may be explained by the larger number of adsorbed CO_2 that leads to hindrance of the motion of N_2 and O_2.

The membrane selectivity $\alpha_{M,\mu,\nu}$ which is defined to be

Table 5

Self-diffusion coefficients (resulting under the rigid-lattice approximation) in the ternary mixtures of CH_4 and CO_2 with air (*i.e.* N_2 and O_2) in ZIF-78 with a ratio of 0.1 of the molecule numbers CH_4/N_2 and CO_2/N_2.

Guest molecule	D_s [m^2/s]		
	228 K	258 K	298 K
$CH_4/N_2/O_2$			
CH_4	0.32×10^{-10}	0.51×10^{-10}	0.89×10^{-10}
N_2	0.70×10^{-10}	1.17×10^{-10}	1.89×10^{-10}
O_2	1.10×10^{-10}	1.96×10^{-10}	4.10×10^{-10}
$CO_2/N_2/O_2$			
CO_2	0.32×10^{-10}	0.48×10^{-10}	0.81×10^{-10}
N_2	0.48×10^{-10}	0.70×10^{-10}	1.94×10^{-10}
O_2	0.68×10^{-10}	1.93×10^{-10}	4.12×10^{-10}

Table 6

Selectivities of CH_4/air and CO_2/air. membrane selectivity = diffusion selectivity x adsorption selectivity in ZIF-78 with a ratio of 0.1 of the molecule numbers CH_2/N_2 and CO_2/N_2, respectively.

Selectivity at 1 bar	Temperature (K)		
	228	258	298
CH_4/N_2			
Diffusion selectivity	0.45	0.43	0.47
Adsorption selectivity	5.65	4.56	3.52
membrane selectivity	2.54	1.96	1.65
CO_2/N_2			
Diffusion selectivity	0.67	0.68	0.42
Adsorption selectivity	90.30	62.90	31.70
membrane selectivity	60.50	42.77	13.31

$$\alpha_{M,\mu,\nu} = \alpha_{A,\mu,\nu} \cdot \alpha_{D_s,\mu,\nu} \tag{8}$$

can be calculated from the adsorption selectivity and the diffusion selectivity. Table 6 summarizes the thus determined data.

The membrane selectivity CH_4/N_2 is about 2.54. The membrane selectivity CO_2/N_2 is around 60.5 at 228 K, 42.77 at 258 K and 13.31 at 298 K.

4. Conclusions

The adsorption and diffusion of CO_2 and of CH_4 on ZIF-78 have been investigated in the pressure region up to 4.5 bar. For 228 K the adsorption of CO_2 has, at 1 bar, almost reached saturation. In contrast, the uptake of N_2 and O_2 seems to be far from saturation, even in the mixture when CO_2 is filling some space in the cavities. Hence, the selectivity is expected to become smaller if the pressure is increased up to *e.g.* 6–10 bar, *i.e.* to the value usually used in technical pressure swing adsorption.

A very high adsorption selectivity of up to more than 140 for the separation of CO_2 and a moderate adsorption selectivity (up to 6.0) for the separation of CH_4 from polluted air by adsorption in ZIF-78 have been found. In both cases the adsorption selectivity is increasing with decreasing temperatures.

It is shown that the N_2/O_2 ratio is found to be nearly the same in the gas phase and adsorbed phase in all mixture simulations of this paper.

Decrease of the temperature increases the adsorption selectivity drastically. Therefore a temperature swing method for separation processes appears to be attractive. Because also a decrease of the pressure increases the selectivity, a simple decompression of the feed gas that leads to both lower temperature and pressure might be an interesting way to be considered.

The CO_2/N_2 selectivity for lower concentration, particularly at 228 K, is higher than for higher concentrations. This increase of the selectivity with decrease of the CO_2 concentration makes ZIF-78 particularly interesting for removing even small amounts of CO_2 from air. Just this is the case where one may easily get into troubles with other techniques.

For the separation of CO_2 from air, techniques based on mere adsorption appear to be more promising than those based on membrane separation, the more since they operate even for high dilution more effectively than for higher pollution. For the separation of CH_4/air mixtures, techniques based on adsorption and techniques based on permeation seem to work both with moderate selectivity.

Preferred adsorption sites for CO_2 in the case of the CO_2/air mixture at 228 K and 1.26 bar are close to the oxygen atom of the lattice while those for CH_4, in the case of the CH_4/air mixture, at 228 K and 1.26 bar, were found to be close to the hydrogen atom of the linker.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.micromeso.2018.07.023.

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Separation of nitrogen dioxide from the gas mixture with nitrogen by use of ZIF materials; computer simulation studies

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ABSTRACT

The separation of nitrogen dioxide (NO_2) from the gas mixture with nitrogen (N_2) by selective adsorption and diffusion in three Zeolitic Imidazolate Frameworks (ZIFs) is examined by Gibbs Ensemble Monte Carlo (GEMC) and Molecular Dynamics (MD) computer simulations at 373 K, which is a temperature that can be found in the exhaust gases of combustion engines and furnaces. This temperature ensures that the chemical equilibrium reaction between NO_2 and N_2O_4 can be neglected since at this temperature almost only NO_2 exists. At 373 K, the membrane selectivity of NO_2 over N_2 is predicted to be about 4.2 (ZIF-90), 5.2 (ZIF-8), and 10.6 (ZIF-78). In addition, it is shown that N_2O_4 can be neither adsorbed nor diffuses inside these ZIF materials, which makes these ZIFs a promising materials for separation by membranes. Due to molecular sieving, only N_2 and NO_2 can pass the ZIF membranes.

1. Introduction

The nitrogen oxides NOx, including nitrogen dioxide NO_2, nitrogen monoxide NO, and dinitrogen tetroxide N_2O_4, belong to the most prominent air pollutants that cause environmental pollution and represent a health risk for humans and animals [1]. If oxygen is available, NO will quickly convert to NO_2. Thus NO_2 and N_2O_4 are the most important representatives of the NOx family. Nitrogen oxides are formed in nature e.g. by bacterial respiration, volcanos, and lightenings. More important is their emission from industrial processes and from combustion engines burning fossil fuels. The percentage of nitrogen oxides in the air is carefully monitored by international organizations. It constitutes one reason for blocking cars from accessing city centers to protect air quality. The removal of NO_x from mixtures of exhaust gases by common technical processes like condensation may not be sufficient to fulfill emission limit values and the creation of low temperatures needed for condensation requires additional efforts and causes energy losses.

Therefore, in this paper we intend to study a possible use of some Zeolitic Immidazolate Frameworks (ZIFs) to remove NO_2 from a N_2/NO_2 mixture by adsorption or membrane separation. ZIFs, as a subfamily of Metal-Organic Frameworks (MOFs), are well known as promising adsorption materials because of their relative high thermal and chemical stability in comparison with other MOFs [2].

N_2 is the main component of air. Moreover, in [3] it has been shown that the adsorption properties of N_2 and O_2 in ZIF-78 are almost identical. In the present paper it is shown that also for the other ZIFs investigated here at 373 K the adsorption isotherms of N_2 and O_2 are very close. Thus, the adsorption of NO_2 from the mixture with N_2 is representative of the adsorption of NO_2 from air in these ZIFs.

We have chosen 3 well known ZIFs that are also well examined regarding the adsorption and diffusion of small guest molecules. ZIF-8 is sold by industrial companies and it was examined in many experimental and simulation papers (see e.g. [4–6]). ZIF-90 has also been examined with respect to gas separation in several papers (e.g. [7,8]), because its average window size is (like that of ZIF-8) close to the size of technically important molecules (CH_4, N_2, CO_2, NO_2 and others). ZIF-78 showed outstanding adsorption selectivity for the separation of CO_2 from air [3]. Thus the question if it can also be used for the N_2/NO_2 separation will be examined in this paper. However, the investigation of the system NO_2/N_2 is delicate, since NO_2 at ambient conditions can be

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found only in a reaction equilibrium with N_2O_4. The partial pressure of NO_2 in the NO_2/N_2O_4 mixture at 1 bar total pressure as a function of the temperature, resulting from the reaction equilibrium, can be seen in Fig. 2 of the supporting material. At 1 bar total pressure and 273 K, the partial pressure of NO_2 in a NO_2/N_2O_4 mixture is only 0.13 bar. However, at 373 K it is 0.96 bar and at 400 K it would even be more than 0.99 bar. Both NO_2 and N_2O_4 are toxic.

In this paper we restrict ourselves to ZIF materials with small pores because the selectivity for the separation CO_2/air was found to be high for ZIF-78 having small pores [3]. A promising way to scan several materials for the N_2/NO_2 separation cheaply and without health risk seems to be computer simulation [9,10] of adsorption and diffusion of NO_2, pure and in mixtures, in such materials. Particularly because of restrictions that apply to experiments with dangerous substances, computer simulations can help to avoid unnecessary experiments. A few papers about NO_x adsorption in special cases can be found in the literature. In [11] 14 porous materials, including several MOFs and zeolites, are investigated with respect to removal of SO_2 and NO_x from flue gas. The flue gas was represented by a mixture of CO_2, N_2, O_2 and H_2O. These investigations have been done at 1 bar and 313 K. In [12] the competitive co-adsorption of CO_2 with H_2O, NH_3, SO_2, NO, NO_2, N_2, O_2, and CH_4 in MOF-74 is considered and the role of hydrogen bonding is examined. In [13,14] palm shell activated carbon (PSAC) for simultaneous removal of SO_2 and NO_x from flue has been examined at 100 °C. In [15] the adsorption of N_2, CO_2, CO, NO in several materials was measured at 273–398 K. The natural zeolite clinoptilolite showed promising selectivities for the separation of NO from N_2. If these results are to be extended to the separation of NO from air, then it must be taken into account that in the presence of oxygen NO will be converted into NO_2 and that, at least at the lower part of this temperature range, a part of the NO_2 will be converted to N_2O_4.

Neither experimental nor simulation papers about the selective adsorption of NO_2/N_2 in MOFs at higher temperatures and at different pressures seem to exist in the literature. The role of the chemical reaction NO_2/N_2O_4 for the adsorption process at lower temperatures has not yet been examined.

For the choice of the 3 ZIF materials we took into account the following considerations: a) Porous materials with strong attractive centers, like open metal centers, could have high adsorption capacity and selectivity. However, they have the disadvantage that the adsorbed molecules can be removed only with very high energy efforts in regeneration. Thus their use is restricted. b) We have found high selectivity for CO_2 in ZIF-78 [3]. Hence we decided to explore ZIF-78 and some similar ZIFs.

Another question is, whether water can influence the adsorption process, yet water can be neglected if the gas to be purified can be dried before.

N_2O_4 molecules are too large to pass the windows that connect adjacent cavities in the ZIFs under study. On the other hand, the cavities themselves are larger than the N_2O_4 molecules and hence dimerization of two NO_2 molecules to a N_2O_4 molecule within a cavity cannot be excluded. Therefore, we investigated the NO_2/N_2 mixture at 373 K where N_2O_4 will exist only in small percentage. NO_2 can be a product of combustion machines that work at even higher temperatures than 373 K and the emitted exhaust gas can have this temperature. At 373 K the N_2O_4 molecules have a short lifetime. If an N_2O_4 will be formed by dimerization within the cavities of a MOF, then it will influence only short time the adsorption/diffusion patterns before it disappears, even if the probability of formation can be somewhat increased by restricted space and higher pressure. An overview over the reaction equilibrium in the gas phase of this reaction using reaction constants from the literature is given in the Supporting Material.

High throughput computer simulation studies consider many (up to several hundred) MOFs in one batch (see e.g. [16–19]). Such studies are a useful and necessary tool with the merit to obtain an overview over the large number of existing and possible MOF structures. This examination, however, treats each MOF individually. This has two main reasons: On one hand simulations of a lot of MOFs in one project can be done only with rigid lattice. In [5] it has been shown that this simplification can lead to diffusion selectivities wrong by up to 5 orders of magnitude. Hence, in the present work the examination of diffusion by MD will be done with flexible lattice even though this requires a larger computational and programming effort (e.g. about 10,000 data lines have to be written in the input file for the simulation package DL_POLY to define the bonded interactions (stretch bond elasticity, angle bond elasticity and torsional elasticity). Torsion is even a 4 body interaction, which is computationally expensive. In contrast to diffusion the flexibility of the lattice is of minor importance for adsorption if no structural changes, like 'gate opening', occur. Whether such effects appear can be checked e.g. by MD simulations with flexible lattice (see e.g. [6,8]). On the other hand, parameters and charges for the lattice atoms depend upon the nature of the bonds and upon the geometry of the neighborhood of each lattice atom. Hence we have not used the same parameters (e.g. from Dreiding or UFF) in all simulations. Instead, we have used for each type of MOF such parameters, that have been proven to work well for this specific type of MOF.

In order to check the performance of the 3 ZIF materials under consideration first the adsorption of N_2 and NO_2 is investigated separately. These adsorption data obtained from pure gases can be applied also on ideal mixtures at low pressure.

In the linear adsorption regime (Henry's law region) the adsorption is characterized by the following equations

$$N_{ads,i} = k_i p_i \tag{1}$$

$$p_i = N_{gas,i} k_B T/V \tag{2}$$

$$N_{ads,i} = k_i N_{gas,i} \frac{k_B T}{V} \tag{3}$$

$$p = \sum_i p_i = \left(\sum_i N_{gas,i}\right) \frac{k_B T}{V} \tag{4}$$

$$\alpha_{ij}^{adsorption} = Def \frac{N_{ads,i}/N_{ads,j}}{N_{gas,i}/N_{gas,j}} \tag{5}$$

$$\alpha_{ij}^{adsorption} = \frac{k_i}{k_j} \tag{6}$$

$N_{gas,i}$ is the number of gas molecules of kind i in the volume V at the temperature T, k_B is Boltzmanns constant. $N_{ads,i}$ is the number of adsorbed molecules of kind i in a porous solid. p_i is the partial pressure of this kind in the gas around the porous solid and k_i is a specific constant for the adsorption of this species in that porous solid. This constant can be found by measurement or, by computer simulation. k_i will in general strongly depend upon the temperature. It will be larger for lower temperatures.

At temperatures far enough above the condensation temperature, at low pressure the gas will be an ideal gas and also the mixture will be ideal and the partial pressures can be calculated from the ideal gas Eq. (2) even in a mixture. In this linear regime the total pressure is simply the sum of the partial pressures (4).

Eq. (5) is the definition of the adsorption selectivity $\alpha_{ij}^{adsorption}$ for adsorption of two species i and j from a mixture. This definition can be used for non-ideal mixtures as well. Using Eqs. (1)–(5) for low pressure, Eq. (6) results. Interestingly, this selectivity at low pressure does not depend on the concentrations of the species in the mixture and also not on the existence of additional gas components. However, Eq. (6) and the mentioned conclusions are not valid for non-ideal mixtures and at pressures out of the region of validity of Eqs. (1) and (2).

2. Computational details

2.1. Zeolitic Imidazolate Frameworks

Details about the lattice structures and the interaction parameters of the ZIFs used in the present paper are given in the Supporting Material.

2.2. Gibbs ensemble Monte Carlo simulations (GEMC) and Molecular Dynamics (MD) simulations

The adsorption isotherms and adsorption selectivities are evaluated in Gibbs Ensemble Monte Carlo simulations (GEMC) [20,21] with rigid lattice. The basic idea of GEMC is that Monte Carlo simulations are carried out simultaneously in two simulation boxes. Box A contains a gas of given temperature, pressure and composition. Box B consists of the porous materials with adsorbed gas particles. Random exchange of gas particles under well-defined conditions leads to thermodynamic equilibrium between the boxes that can be analyzed. The method is described in detail in the supporting material of [3]. A home-made software, called Gibbon is employed that was successfully used in several previous papers [3,6–8,22,23].

The Molecular Dynamics simulations (MD) [9,10] have been carried out with the DL_POLY 2.20 package. The numbers of guest molecules for a given pressure are taken from the GEMC simulations. The simulation time step was 2 fs. For each run the system was first relaxed and adjusted to the desired temperature during 5 ns in the NVT (canonical) ensemble. But, for the evaluation part of the run the simulations were done in the NVE (microcanonical) ensemble in order to avoid artefacts from thermalization. The duration of the NVE runs was 25 ns for ZIF-8 and ZIF-90 and 5 ns for ZIF-78. For the test with N_2O_4 (Fig. 11) the NVE for ZIF-78 was 10 ns.

2.3. Mean square displacement (MSD)

The self-diffusion coefficient D_s is related to the particle movements by the mean square displacement (MSD) [9,24] for large times t

$$<(\boldsymbol{r}(t) - \boldsymbol{r}(0))^2> \; = \; 6D_s t \tag{7}$$

$\boldsymbol{r}$ is the position vector. $(\boldsymbol{r}(t) - \boldsymbol{r}(0))^2$ is the square of the distance travelled by a given particle during the time t and $< \ldots >$ means averaging over all particles and many time origins. From the slope of the MSD as a function of time the self-diffusion coefficient (D_s) is obtained. Simulations of the self-diffusion of NO_2 at 373 K have been performed. After an initial equilibration run 25,800,000 simulation steps have been done in order to calculate the MSD. These MD simulations for ZIF-8 and ZIF-90 were done with flexible lattice and the simulation box contained 2 × 2 × 2 unit cells. After the equilibration of the system in the NVT ensemble (Nose-Hoover thermostat) the evaluations have been done in the NVE ensemble in order not to bias the results by artefacts coming from the thermostat.

In ZIF-8, 16 N_2 molecules and 6 NO_2 molecules have been included. This corresponds to the average loading at 373 K and 10 bar found in the GEMC simulations. For lower pressure the number of adsorbed particles would be too small for reasonable statistics. In ZIF-90, 12 N_2 molecules and 4 NO_2 molecules have been included, also corresponding to 10 bar.

The evaluation of the MSD in ZIF-78 was done with rigid lattice in an MD box containing 4x4x4 unit cells. The rigid lattice is justified by the large window diameter of 4.4 A in ZIF-78 (in comparison to 3.4 A in ZIF-8 and 3.5 A in ZIF-90) because the influence of the lattice flexibility results mainly from window passages of the molecules and it is small for windows that are larger than the kinetic diameters of the molecules under consideration. The simulations have been performed with 213 N_2 molecules and 124 NO_2 molecules according to the adsorption results at 10 bar.

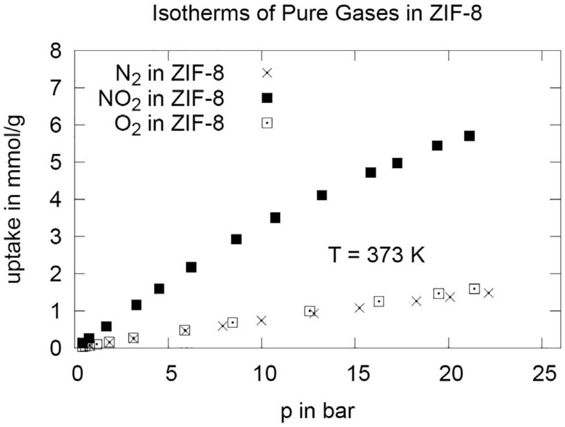

Fig. 1. Adsorption isotherms of pure N_2 and NO_2 as well as O_2 in ZIF-8 at 373 K.

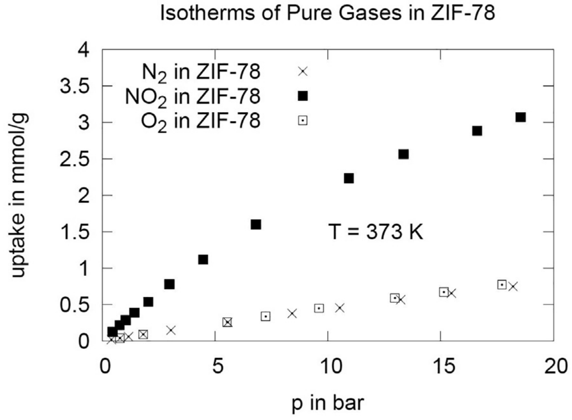

Fig. 2. Adsorption isotherms of pure $N_{2,}$ O_2 and NO_2 in ZIF-78 at 373 K.

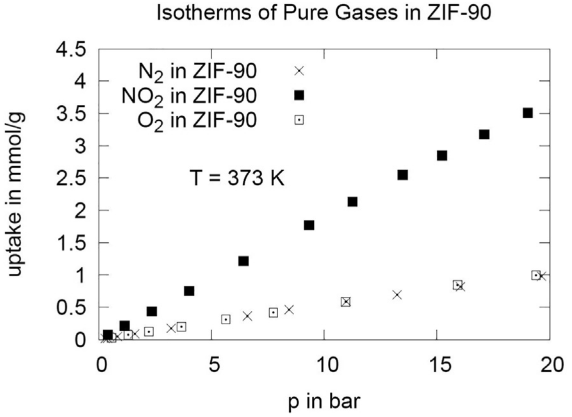

Fig. 3. Adsorption isotherms of pure $N_{2,}$ O_2,and NO_2 in ZIF-90 at 373 K.

3. Results and discussion

3.1. Adsorption of pure gases in ZIF-8, ZIF-78 and ZIF-90

As mentioned above, the adsorption of pure $N_{2,}$ NO_2 and O_2 gas was first investigated. The results are given in Figs. 1–3.

Oxygen was included in order to evaluate the separation of NO_2 from air. It is found that the adsorption isotherm of O_2 is almost identical with that of N_2. This means that the adsorption performance of NO_2 from N_2 will be identical to that of NO_2 from air. A similar observation was made for ZIF-78 at various temperatures in [3]. In [3] it was also shown that in the presence of N_2 and O_2, CO_2 adsorption is

Table 1
Overview over adsorption selectivities and NO_2 uptake at 1 bar and 373 K in the Henry's law region for the 3 ZIFs.

ZIF materials	$\alpha_{ij}^{adsorption}$	NO_2 uptake in mmol/g
ZIF-8	4.25	0.34
ZIF-90	3.23	0.19
ZIF-78	5.57	0.28

comparable. Table 1 shows the NO_2/N_2 selectivity calculated from Eq. (5) and the amount of NO_2 adsorbed at 1 bar.

3.2. Adsorption of the mixture NO_2/N_2 at pressures up to 25 bar in ZIF-8, ZIF-78 and ZIF-90

At higher pressures the mixed gas adsorption selectivity cannot be calculated by Eq. (6) from the adsorption of the pure gases. Its calculation from adsorption data of pure substances would in principle be possible by Ideal Adsorbed Solution Theory (IAST) but, we have chosen the direct way, namely to simulate the mixture itself.

Because of poor statistics for small particle numbers we could not investigate very low NO_2 concentrations in the mixture. Therefore, we have chosen the numbers of N_2 and NO_2 molecules in box A (which contains the free gas outside the ZIF) to a ratio of 10:1. The NO_2 molecules are therefore 9.1% of all molecules in the mixture. This ratio had to be adjusted by trial and error runs with varying particle numbers and box sizes.

Including O_2 in order to examine air, as it was done in [3], would make the simulation more difficult and expensive. Moreover, in [3] it turned out that, with respect to the separation of CO_2 from air, the air behaved similar to pure N_2. This is to be expected also for the case of the separation of NO_2 from air.

Fig. 4 shows the adsorption isotherms of both kinds of molecules in this mixture in ZIF-8. It may look contra-intuitive that more N_2 than NO_2 molecules are adsorbed, but, the ratio in the gas is 10:1 and if the selectivity would be equal to 1, then the amount of N_2 within the ZIF should be ten times that of NO_2.

The selectivity as defined in Eq. (5) for this mixture in ZIF-8 is given in Fig. 5.

The adsorption selectivity of ZIF-8 for NO_2/N_2 seems to increase slightly with increasing pressure, but the increase, if any, is within the range of the fluctuations.

Fig. 6 shows the adsorption isotherms for the NO_2/N_2 mixture in ZIF-90. The investigations have not been extended to lower pressures because at 5 bar there are, on average, only about 3 molecules of NO_2 in the simulation box that contains the ZIF, and because of fluctuations quite often the ZIF does not contain any NO_2.

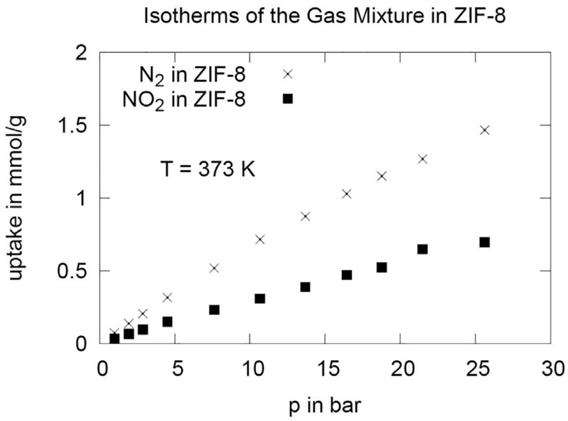

Fig. 4. Mixed gas adsorption isotherms NO_2/N_2 in ZIF-8 at 373 K. The ratio of NO_2:N_2 in the gas phase was 1:10, i.e. the NO_2 content thus 9.1 vol%.

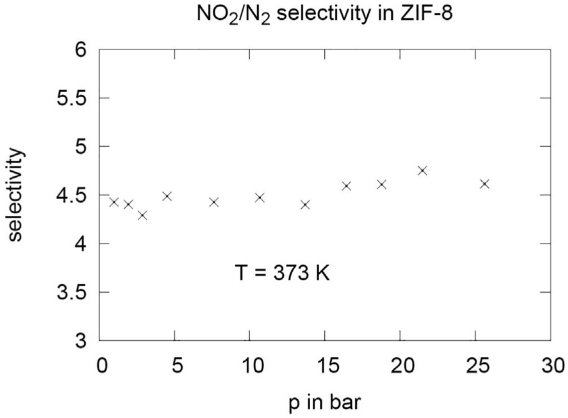

Fig. 5. Adsorption selectivity for the mixture NO_2/N_2 in ZIF-8 at 373 K. Data from Fig. 4.

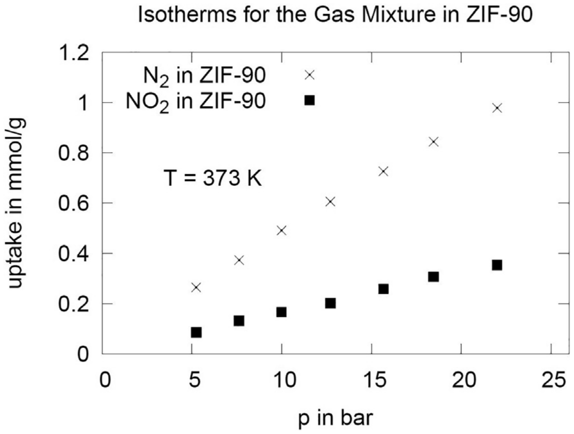

Fig. 6. Mixed gas adsorption isotherms NO_2/N_2 in ZIF-90 at 373 K. The ratio of NO_2:N_2 in the gas phase is 1:10, i.e. the NO_2 content is 9.1 vol%.

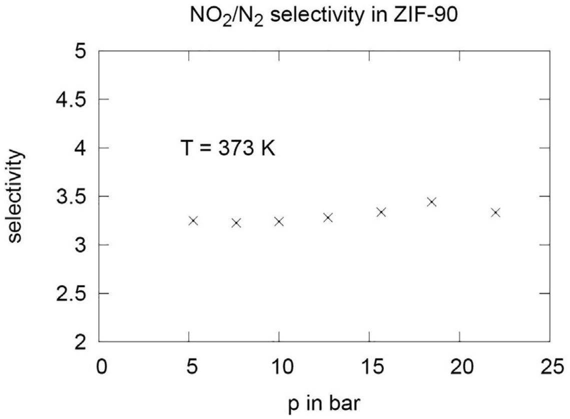

Fig. 7. Adsorption selectivity for the mixture of N_2 and NO_2 in ZIF-90 at 373 K. Data from Fig. 6.

The selectivity as defined in Eq. (5) for this mixture in ZIF-90 is given in Fig. 7.

Like for ZIF-8, a small increase of the adsorption selectivity with increasing pressure within the range of fluctuations, cannot be excluded also for ZIF-90.

Fig. 8 shows the adsorption isotherms of both components of the mixture of N_2 and NO_2 in ZIF-78 at 373 K. The content of NO_2 in the connected gas phase was again 10 per cent of that of N_2. As already observed in [3] for the adsorption of CO_2 also for NO_2 the fluctuations

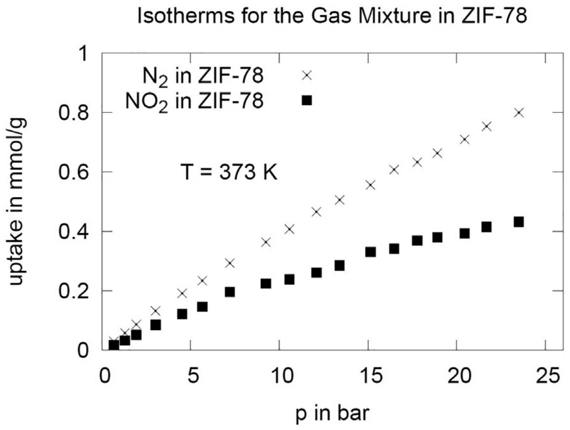

Fig. 8. Mixed gas adsorption isotherms NO_2/N_2 in ZIF-78 at 373 K. The ratio of NO_2:N_2 in the gas phase is 1:10, i.e. the NO_2 content is 9.1 vol%.

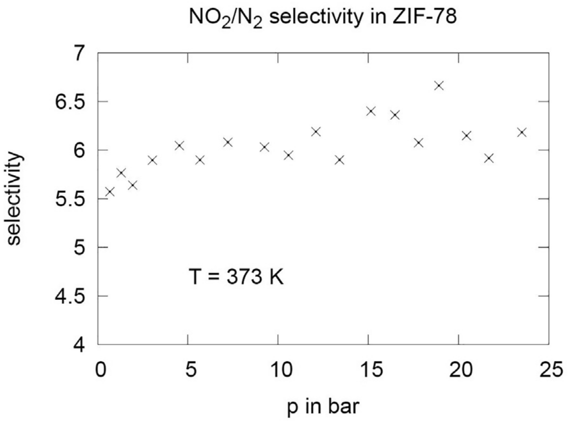

Fig. 9. Adsorption selectivity for the mixture of NO_2/N_2 in ZIF-78 at 373 K. Data from Fig. 8.

for adsorption in ZIF-78 are quite big. This was the main reason to extend the GEMC simulations for ZIF-78 to a larger simulation box and more particles in comparison to the other ZIFs in order to improve the statistics. These fluctuations lead to the scattering of the data for the adsorption selectivity that can be seen in Fig. 9.

3.3. Self–diffusion coefficients of NO_2 and N_2 in the mixture at 373 K at 10 bar

The self-diffusion coefficients D_s of NO_2 and N_2 in the mixture at 373 K for the three materials can be seen in Table 2.

Fig. 10 shows a comparison of the self-diffusion coefficients of N_2 and NO_2 in the adsorbed N_2/NO_2 mixture in the three ZIF materials at 10 bar and 373 K. The shifts of one N atom in N_2 and of the N atom in NO_2 have been used for these calculations because the small size of the two molecules and the much larger shifts allow this simplification. The resulting error is smaller than the fluctuations in the MSD.

It can be seen that the self-diffusion of both components in ZIF-78 is considerably smaller than in ZIF-8 and ZIF-90.

Table 2
The self-diffusion coefficients D_s of the N_2/NO_2 mixture in ZIF materials at 373 K.

ZIFs materials	D_s of N_2	D_s of NO_2
ZIF8	6.33×10^{-10}	7.30×10^{-10}
ZIF78	3.19×10^{-10}	1.80×10^{-10}
ZIF90	1.53×10^{-9}	1.94×10^{-9}

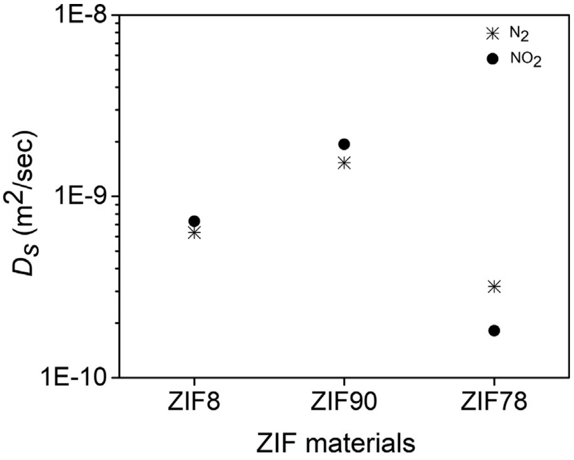

Fig. 10. The self-diffusion coefficients D_s of N_2 and NO_2 in the N_2/NO_2 mixture in the three ZIF materials at 10 bar and 373 K.

This can be important for the flow through a membrane for separation purposes.

Using the results from GEMC and MD the different selectivities, as defined in formulas (5), (9), (10), can be calculated. Table 3 shows these selectivities.

The effectivity of separation processes can be expressed by the selectivities. They are defined as

$$\alpha_{ij}^{\text{diffusion}} = D_j^{\text{diffusion}}/D_i^{\text{diffusion}} \tag{9}$$

$$\alpha_{i\,j}^{\text{membrane}} = \alpha_{ij}^{\text{adsorption}}\,\text{x}\,\alpha_{ij}^{\text{diffusion}} \tag{10}$$

The adsorption selectivity $\alpha_{ij}^{\text{adsorption}}$ was defined in Eq. (5). D_i and D_j are the self-diffusion coefficients of kind i and j. The membrane selectivity is the product of the adsorption selectivity and the diffusion selectivity.

3.4. Some remarks about membrane separation of N_2O_4 from air at room temperature

In a mixture, containing only NO_2 and N_2O_4 at 1 bar and room temperature, the NO_2 content will be about 25%. Lower pressure will shift the NO_2/N_2O_4 equilibrium in favor of NO_2. For the mixture N_2/NO_x at 1 bar the partial pressure of NO_x will be smaller than 1 bar. Thus the ratio of NO_2 to N_2O_4 will be larger than 1:4. To assess this quantitatively, the chemical reaction NO_2/N_2O_4 must be included in the treatment. This can be done by so called RxMC simulations [25–27]. Such simulations are in preparation and will be the subject of another paper.

The present paper is, therefore, restricted to 373 K. One interesting aspect of the membrane selectivity at both low and high temperature can, however, be considered without reaction simulations: We checked in MD simulations with flexible lattice whether the bulky molecule N_2O_4 can diffuse within the ZIFs examined. If it cannot diffuse at 373 K, then the chance that it can diffuse at lower temperatures is zero. These considerations concerning a few isolated N_2O_4 molecules are independent of the composition of the gas outside of the ZIF.

Fig. 11 shows the time evolution of the MSD in the three materials, showing that N_2O_4 can neither penetrate nor diffuse in any of the ZIFs under study which indicates that no passage through such membranes should be possible.

For the MD simulations, a few N_2O_4 molecules have been put into the cavities of the ZIFs. The space within the cavities is sufficient even if the molecules in cannot pass the windows to come to these positions. If NO_2 molecules had penetrated into these cavities, some N_2O_4 molecules could be formed there by dimerization. However, in the following the simulation can be considered as thought experiment independently of

Table 3
The adsorption selectivity, diffusion selectivity and membrane selectivity of the mixture N_2/NO_2 in ZIF materials at 10 bar at 373 K.

ZIF materials	Adsorption selectivity ($\alpha_{ij}^{adsorption}$)	Diffusion selectivity ($\alpha_{ij}^{diffusion}$)	Membrane selectivity ($\alpha_{ij}^{membrane}$)
ZIF-8	4.5	1.15	5.2
ZIF-90	3.3	1.27	4.2
ZIF-78	6.0	1.77	10.6

the source of N_2O_4 molecules in the cavity.

Taking into account that the cavity diameters are between 7 and 10 Å their squares are between 49 and 100 Å^2. That means that the MSD must be larger than these values in order to indicate movements that lead beyond the cavity where the particle was situated at $t = 0$. That is to say that the root MSD seems to become limited to the diameter of the large cavities. Fig. 11 clearly shows that the diffusion of N_2O_4 through the ZIFs under study is negligible. The slope of the MSD as a function of time vanishes (except fluctuations) before the square of the cavity diameter is reached. Thus, at 300 K where many NO_x are present as N_2O_4, a much higher membrane selectivity is to be expected than at 373 K, where the NO_x molecules mainly exist in form of NO_2.

4. Conclusions

Our computer simulations show that the adsorptive separation of NO_2/N_2 mixtures by zeolitic imidazolates frameworks (ZIFs) is possible.

The adsorption selectivities are moderately, high but will become larger at lower temperatures. At 373 K ZIF-78 has the highest membrane selectivity of NO_2 over N_2, almost 11, hence, this paper is to be understood as a first step toward further investigations that include lower temperatures. However, at temperatures between 373 K and room temperature (RT), the influence of the different NO_x dissociation–recombination reactions must be taken into account. For these future studies, the implementation of the aforementioned RxMC method will be necessary and this is already in preparation, to be included into our Gibbon software, that was described in the computational details. At RT, NO_x is present as N_2O_4 the mole fraction of NO_2 molecules will be quite small. The bulky N_2O_4 molecules can be effectively separated from air by using any of the 3 ZIFs under study as molecular sieve membrane. Different from the adsorptive separation, membranes are expected to show a much higher N_2/NO_x/selectivity at RT due to molecular sieving.

CRediT authorship contribution statement

T. Chokbunpiam: Conceptualization, Project administration, Data curation, Investigation, Writing - original draft. **R. Chanajaree:** Investigation, Data curation. **J. Caro:** Supervision. **W. Janke:** Supervision. **T. Remsungnen:** Supervision. **S. Hannongbua:** Supervision. **S. Fritzsche:** Methodology, Software, Investigation, Data curation, Validation, Supervision.

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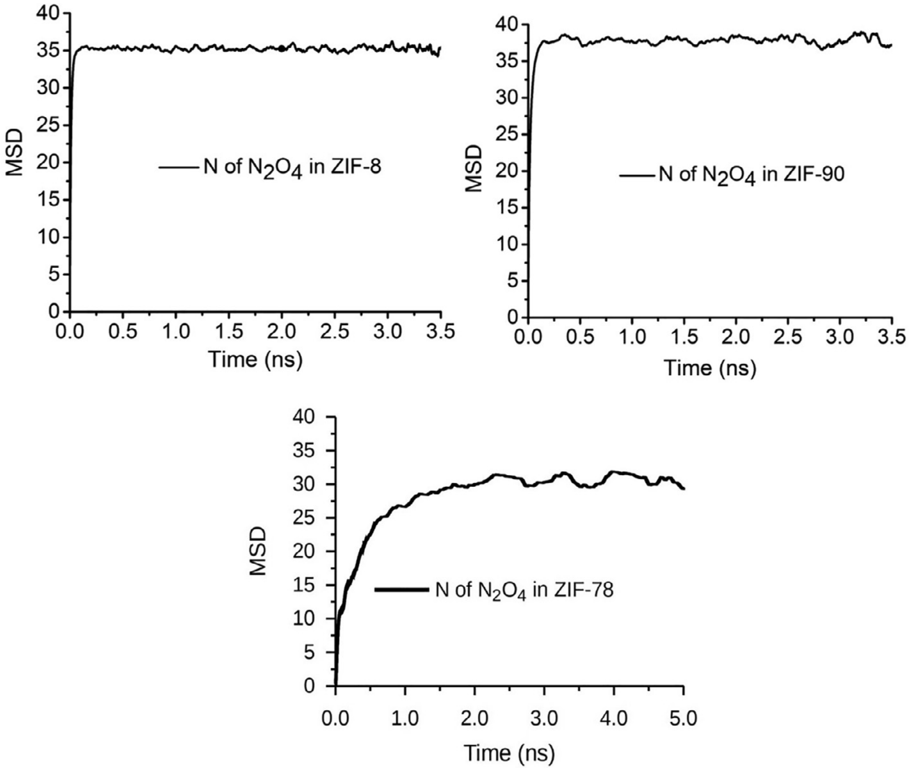

Fig. 11. The mean square displacement of an N atom in the N_2O_4 molecule for movements within the different ZIFs assuming flexible lattice.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.commatsci.2019.05.025.

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REGULAR ARTICLE

CO_2 induced swing effect at imidazolate of zeolitic imidazolate framework-90 using molecular simulations

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Abstract
The influence of adsorbed CO_2 molecules on the lattice structure of ZIF-90 has been examined. Parameters verified by adsorption simulations have been used. Two lattice structures corresponding to so-called gate opening can be observed depending upon the amount of adsorbed guest molecules and the temperature. A transition region has been found in which both of the structures appear temporarily leading to broad statistical distributions of window diameters. Diameters up to 4.43 Å are found. An increased window diameter is observed at high temperature even for the empty lattice.

Keywords Zeolitic imidazolate framework-90 (ZIF-90) · Gate opening · CO_2 · Adsorption · Diffusion · Molecular simulations

1 Introduction

A new subclass of MOFs which has zeolitic structure called zeolitic imidazolate frameworks (ZIFs) has been synthesized [1]. Having good properties of both MOFs and zeolites, not only inherent properties, large surface areas, pore volume, but also an excellent chemical and thermal stability, it is not surprise that ZIFs are emerging in material research in recent years. Since the lattice flexibility of these materials (see, e.g., [2–5]) is a key factor in many applications, it should be understood clearly. One of the physical phenomena in flexible porous materials is gate opening that depends on many factors such as species of the adsorbed molecules, amount of adsorbed molecules, pressure and/or temperature. The investigation of gate opening of several MOFs can provide better understanding of adsorption and diffusion. These outcomes have impact on performance of ZIFs in the industrial separation process. A well-known example for lattice flexibility is ZIF-8. The flexibility of the structure of ZIF-8 relies on the methyl-imidazolate linker. The experimental nitrogen adsorption isotherm of ZIF-8 at 77 K shows two steps at a very high pressure (1.47 GPa) because of a swing effect in the imidazolate linker [6]. ZIF-8 was approved to show gate opening in presence of different small gases molecules for instance, C_2H_6 [7] and high loading of CO_2 [8]. In contrast such an effect has not yet been reported for ZIF-90.

ZIF-90 was firstly discovered by Yaghi et al., in 2008 [1]. It has the same topology as ZIF-8 but the substituent is changed from the CH_3 group in the imidazolate to a CHO group. It shows outstanding separation performance with size-selective capability derived from its pore size of 3.5 Å [1]. It is composed of tetrahedral metal ion (ZnN_4) with linker imidazolate-2-carboxyaldehyde (Ica). There are two types of apertures which are composed of four linkers (four-membered ring) and six linkers (six-membered ring) in

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Fig. 1. The largest cavity diameter is 11.0 Å and the window size (six-membered ring) is 3.5 Å.

The combination of high-pressure (HP) single-crystal diffraction and computational study on ZIFs demonstrates that ZIF-8, ZIF-90, and ZIF-65 were found to show gate opening in a MeOH/EtOH (4:1) mixture at pressures of 1.47, 0.88, and 0.73 GPa, respectively, and the phenomena of linker rotation caused by guest–framework interaction [9]. Moreover, the MD simulations of an H_2/CH_4 mixture showed the gate opening from 3.55 to 3.73 Å in ZIF-90 at high temperature [5]. For CO_2, there are reports about a gate-opening effect for ZIF-8 in contrast with ZIF-90.

The aim of this work is to investigate the gate opening in ZIF-90 as a function of the number of CO_2 and of the temperature. First, adsorption isotherms are investigated using Gibbs ensemble Monte Carlo (GEMC) simulations with different force fields, and then the results are compared with the experiment in order to find the appropriate force field for CO_2 in ZIF-90. Then, the effects of the number of CO_2 and temperature were examined by using molecular dynamics simulations. The flexibility of the ZIF structure has important influence on the diffusivity of gases through their frameworks. Therefore, the structural changes have been examined during all of the MD simulations.

2 Simulation details

2.1 Interaction potentials

The intermolecular potential in GEMC can be expressed as the sum of atom–atom Lennard-Jones (LJ) potentials U_{LJ} and Coulomb interactions U_{coul} defined for each pair ij of atoms (that means atoms in guest molecules or of the lattice) as:

$$U_{\mathrm{LJ}}(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \tag{1}$$

$$U_{\mathrm{coul}}(r_{ij}) = \frac{1}{4\pi\varepsilon}\left(\frac{q_i q_j}{r_{ij}}\right) \tag{2}$$

where r_{ij} is the distance between sites i and j, q_i is the electric charge of atom i, ε_0 is the permittivity of vacuum, ε_{ij} is the LJ energy parameter (depth of the minimum) and σ_{ij} is the LJ diameter for an ij pair. For illustration, see also the supporting material.

The parameters for interaction between unlike atoms are calculated by the Lorentz–Berthelot combining rule as:

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}) \tag{3}$$

and

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii} \cdot \varepsilon_{jj}} \tag{4}$$

2.2 Gibbs ensemble Monte Carlo (GEMC) simulations

The strategy of the paper is the following: First we try to find the most appropriate set of interaction parameters for our system among some sets that are proposed in the literature by comparing calculated adsorption isotherms with experimental ones also found in the literature. Then, we use these optimal parameters for dynamical calculations in molecular dynamics (MD) in order to investigate the influence of the guest molecules on the lattice structure, and we evaluate the self-diffusion coefficient.

First adsorption isotherms of CO_2 in ZIF-90 were calculated by Gibbs ensemble Monte Carlo (GEMC) simulations. A rigid lattice was sufficient since even if the flexibility has strong influence on diffusion, for adsorption it is important only in case of molecules that are larger than the window diameter and that cannot penetrate into the lattice without flexibility or in cases in which the adsorbed gas changes the whole lattice drastically [10]. This is not the case for CO_2 in ZIF-90.

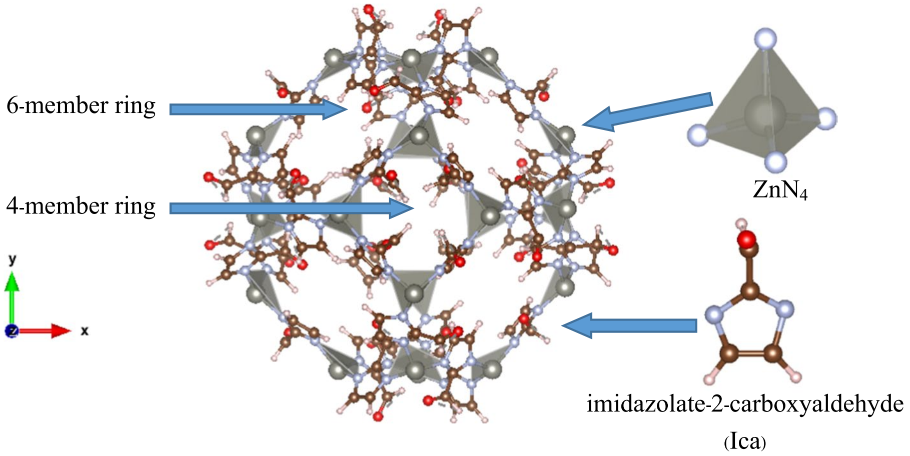


Fig. 1 1-unit cell structure of zeolitic imidazolate framework-90. Zn, gray; O, red; H, pink; N, blue; C, brown

Table 1 Force field parameters of CO_2

Force fields	Atom	σ (Å)	ε (kcal/mol)	q (e)
FF1 (Liu et al. [16])	C	3.43	0.10459	+0.544
	O	3.12	0.05974	−0.272
FF2 (Murthy et al. [17])	C	2.785	0.057629	+0.596
	O	3.014	0.165138	−0.298
FF3 (Potoff et al. [18])	C	2.80	0.05343	+0.70
	O	3.05	0.15634	−0.35
FF4 (Zheng et al. [19])	C	2.757	0.05584	+0.6512
	O	3.033	0.15982	−0.3256

A homemade GEMC software named Gibbon was employed that has been successfully used in [5, 8, 11–15].

The four candidates of CO_2 parameters as given in Table 1 are used to find the suitable force field of CO_2 in the ZIF-90 system at 303 K by a comparison with the experimental data. For the CO_2 molecules, we name the parameter sets that are considered as FF1–FF4. They belong to the common models that are named in the literature as UFF [16] (united force field), MSM [17], TraPPE [18] (transferable potentials for phase equilibria) and EMP2 [19] (elementary physical model 2), respectively. The parameters of the ZIF-90 lattice were taken from the nonbonding potential part of Phuong et al. used in [13].

The Gibbon software performs Metropolis Monte Carlo in two boxes simultaneously in one simulation at desired temperature. Equilibrium between the boxes is achieved by random particle exchange taking account of microscopic reversibility. The gas phase of the desired gas (CO_2) is simulated in box A while box B contains 64 (4×4×4) unit cells of the ZIF-90 with adsorbed gas. Within each box, random displacements and random rotations are carried out ruled by the Metropolis algorithm. The Coulomb interactions (2) are not calculated by Ewald summation, but they are treated with a damping factor for larger distances. Replacing the Ewald sum by such methods is extensively discussed in [21], and our application is described in more detail in [13]. Additionally, the sum of the electrostatic potential contributions of the three point charges of each CO_2 atom is considered as an entity. This is a method analogously to the charge group method [20] for long-range interactions. The faster decaying sum is calculated within distances between the centers of masses of the two molecules smaller than the cutoff radius of 30 Å. By these techniques, the computer time needed in the GEMC simulation is reduced considerably.

2.3 Molecular dynamics (MD) simulations

The simulation box of eight (2×2×2) unit cells of ZIF-90 was assembled from the X-ray structure that was taken from the CCDC database [1]. Because the lattice flexibility plays an important role in calculations of dynamic properties in several MOFs as shown in [5], a force field for a flexible lattice of ZIF-90 was applied in the MD simulations. It was developed by our group and approved in CH_4 adsorption [13]. This force field is presented in supporting information.

The force field of CO_2 was chosen from the best agreement with experiment of the results for adsorption isotherms. This force field was used to explore dynamic properties of the system. The MD simulations have been carried out by use of the DL-POLY classic package. The approximation of nonbonding interaction of two-atom site in both CO_2 and ZIF-90 is described in terms of Lennard-Jones potential. The Lorentz–Berthelot mixing rules were applied to obtain the cross-interactions parameters **σ** and **ε** between two atoms which is described in GEMC part. Adsorbed amounts of CO_2 in the range of 0.5–30 molecules per cage were investigated in five temperature series. All simulations started with NVT ensemble with Nosé–Hoover thermostat for 2 ns to control the temperature. After that NVE ensemble MD simulations were carried out during 25 ns to examine the dynamic properties. The effect of temperature and the amount of gas loading to the swinging of the imidazolate six-membered ring are examined in terms of window diameter distributions. The self-diffusion coefficients of CO_2 in ZIF-90 are evaluated.

3 Results and discussion

3.1 Gibbs ensemble Monte Carlo (GEMC) simulations

The GEMC simulations yield the calculated adsorption isotherms of CO_2 in ZIF-90 at 303 K that are shown in Fig. 2. By comparison of these adsorption isotherms, it turns out that the adsorption isotherm of FF1 (filled square) presents

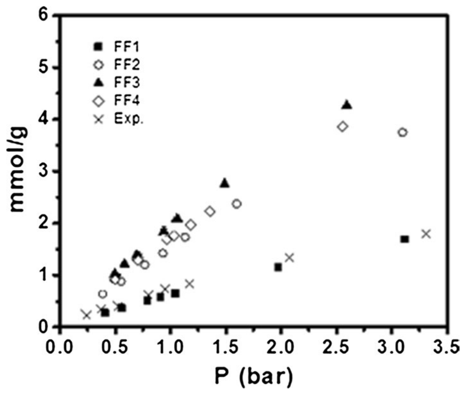


Fig. 2 Calculated adsorption isotherms of CO_2 in ZIF-90 using GEMC (FF1–FF4) compared with experiment (× symbol) [22] at 303 K

good agreement with experiment (x) along the pressure range from 0.5 to 3.5 bar. On the other hand, the other force fields give overestimated adsorption. Hence, the FF1 parameter set, that is, from Liu et al. [16] was selected to be used in the MD simulations.

3.2 Molecular dynamics (MD) simulations

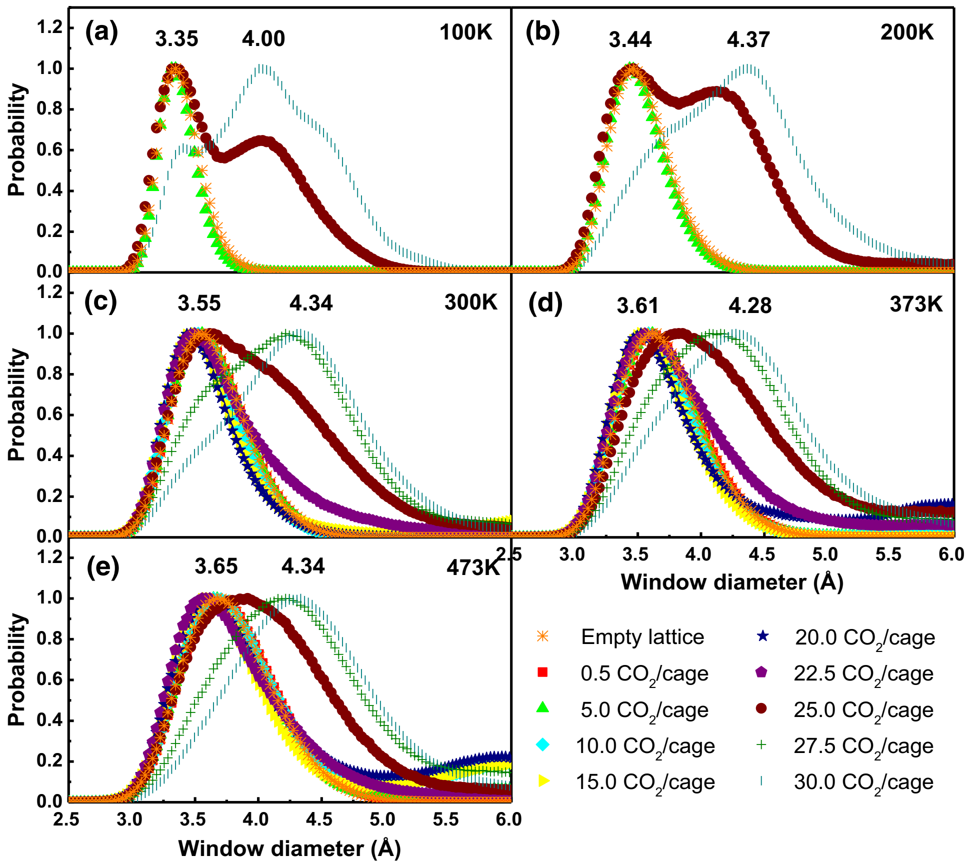
3.2.1 Effect of the number of adsorbed gas molecules

Diffusion of CO_2 and dynamic properties of the ZIF-90 structure were monitored in terms of self-diffusion coefficient and windows diameter, respectively. The distributions of window diameters of the six-membered ring at different temperatures are plotted in Fig. 3. For example at 300 K for loadings from 0.5 to 22.5 CO_2/cage, the diameter distributions of the six-membered ring show a clear peak at around 3.49–3.53 Å. The peak is corresponding to the average experimental data of 3.50 Å [1]. But at 25 CO_2/cage, a very broad peak has been found covering the whole region between 3.61 and 4.25 Å. It can be concluded that there are two phases of structure mixed together showing different forms of rotation of the imidazolate group. The structure with lower window diameter is called "normal stage", and the one with higher window diameter is called "expanded stage." However, for loadings higher than 25 CO_2 the height of the peak of the normal stage region decreases but the peak corresponding to the expanded stage region increases as established at window diameters of 4.22 Å at 27.5 CO_2/cage. Finally, the complete transformation of the structure to the expanded stage occurred at 30 CO_2/cage. It shows the highest peak at 4.34 Å which is a higher value than the one observed in the previous work of ZIF-8 at 4.125 Å by around 0.21 Å. Thus, interestingly, the transition state of normal stage to expanded stage in this CO_2-ZIF-90 system can be observed explicitly in the present work. The CO_2 molecules can induce the transition of the window diameter of ZIF-90 similar to in ZIF-8 [8] but in the previous CH_4-ZIF-90 [13] examination, no structure transition could be seen. For temperatures lower than 300 K, the transition state is less pronounced but a shoulder in the distributions can be seen.

3.2.2 Temperature effect

In Fig. 3, even in the empty lattice (without CO_2 molecules in the framework) window diameters are gradually increased from 3.35 to 3.65 Å when the temperature is increased in the range of 100–473 K. The average window

Fig. 3 Distributions of the window diameter of ZIF-90 for different loadings of CO_2 as well as empty lattice in range of 100–473 K



diameters under 25 CO_2/cage at a temperature range of 100–473 K show the same series like the empty lattice of around 3.35, 3.44, 3.55, 3.61, and 3.65 Å, respectively. At a loading of 30 CO_2/cage, the structures were not completely transformed to the expanded stage at 100 and 200 K because two peaks appear. They are continuously changed to reach the expanded stage at 300 K. The highest value of the window diameter at which a peak in the distribution at the expanded stage appears is 4.34 Å. It can be found at highest temperatures (473 K). This is the highest value which has never been observed before in previous studies of ZIF-8 (300 K) [5].

Let us focus on the point of the first rapid increase in the windows diameters which happens at the same number of guest loading at 25 CO_2/cage for all temperatures. More details about the window diameter for 25 molecules per cage at different temperatures are explained in Fig. 4. At a temperature of 100 K, two characteristic peaks of the window diameter can be observed. The first sharp peak appears at 3.35 Å and the second broad peak at 3.95 Å. When the temperature was increased, the second peak was also increased. Then, it was blended with the first peak into the one very broad peak starting at 300 K. The average window diameters at 300–473 K were shifted from the first peak of 100–200 K (3.35 Å) to around 3.9–4.0 Å.

It is clearly to note that the rotation of the imidazolate is the key of understanding the behavior of the window diameter and can also be induced by temperature changes.

In Fig. 5, the diffusion of CO_2 was gradually increased form 1.65×10^{-10} to 1.90×10^{-10} m^2/s at a loading range 0.5–15 molecules/cage for 300 K and started to decrease at 20 molecules/cage. The D_s was dropped down to 5.04×10^{-12} m^2/s at 30 molecules/cage. This trend is also observed at higher temperatures of 373 and 473 K. The D_s increases with increasing temperature as to be expected because of increased thermal motion. For very high CO_2 content, the mutual hindrance of the CO_2 molecules drops down the mobility.

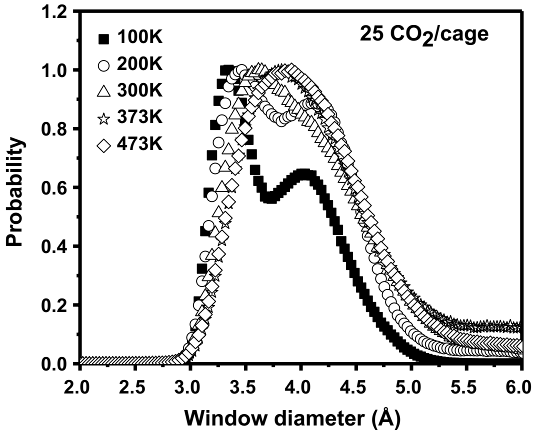


Fig. 4 Distributions of the window diameter at 25 CO_2/cage for five temperatures

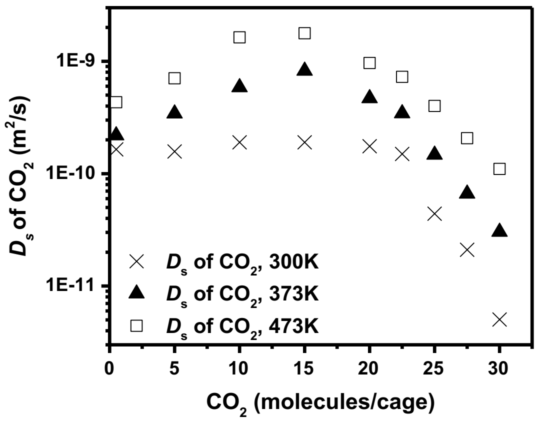


Fig. 5 Calculated D_s for CO_2 loadings of 0.5–30 molecules/cage in ZIF-90 frameworks at 300, 373, and 473 K by MD simulation

3.2.3 Radial distribution functions and density plots

In order to check the distribution of guest molecules within the lattice and to identify adsorption centers, the radial distribution functions (RDFs) and density plots have been examined. Figure 6 shows the pair of correlation functions of atoms of CO_2 with various lattice atoms. It can be seen that the adsorption sites are not at the metal ion, but at the O_OT atom of the linker. It was supported by the density plot in Fig. 7 where the density of CO_2 scatters around the imidazolate-2-carboxyaldehyde linkers at low concentration, while it is stronger at the center of the cage at higher concentration. The preferred orientation of CO_2 is so that the O and C atom of CO_2 is closer to the O_OT atom. As to be expected the adsorption centers are more pronounced at lower temperatures as can be seen in the supporting information.

4 Conclusions

The MD simulations of CO_2 in ZIF-90 at various concentrations and temperatures were examined for finding factors of gate-opening effect and adsorption site. For all simulations, the adsorption sites are located on imidazolate-2-carboxyaldehyde linkers and close to the O_OT atom and all C atom of linkers, respectively.

The gate-opening effect was considered in terms of six-membered ring window diameter distributions. When the numbers of CO_2 are increased from 5 to 30 molecules per

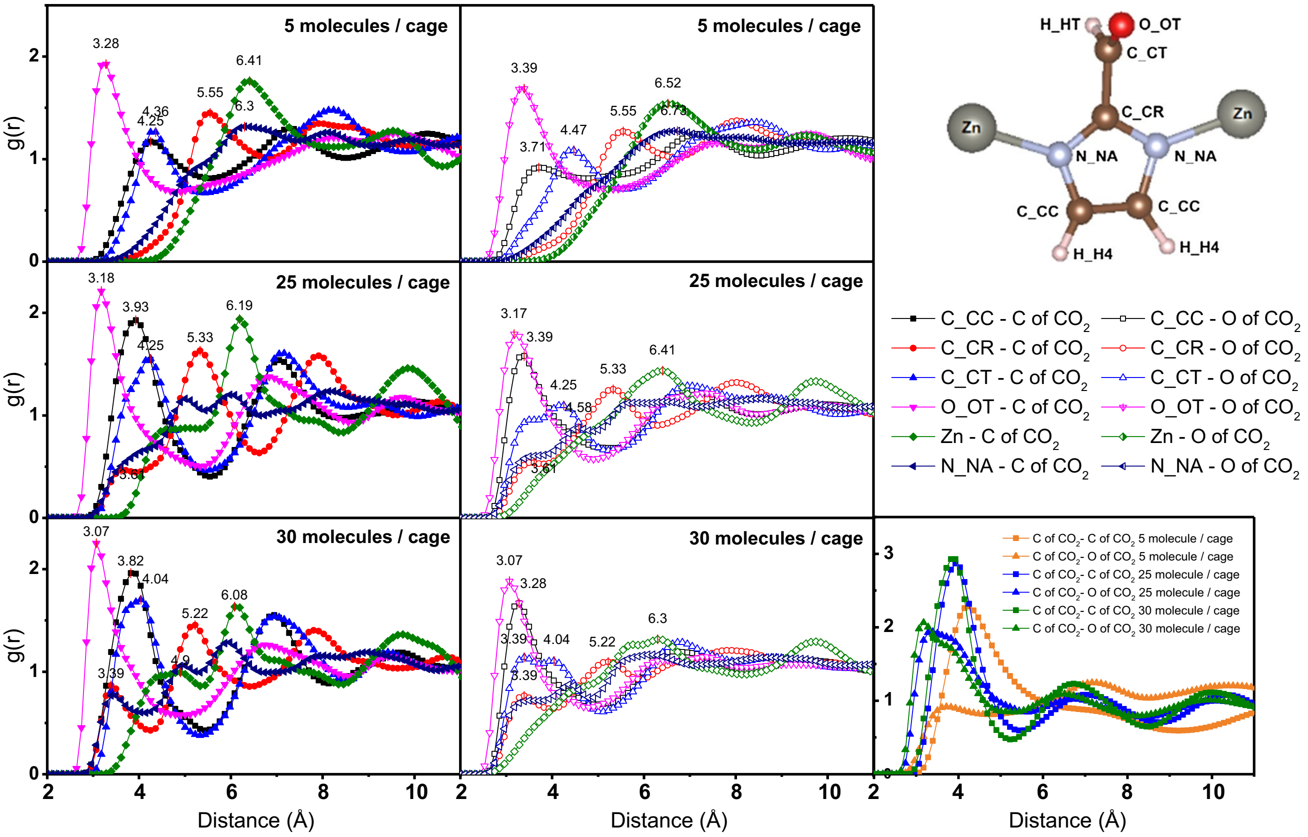


Fig. 6 RDFs of lattice atoms with CO_2 and CO_2 itself at loadings of 5, 25, and 30 molecules/cage in ZIF-90 frameworks at 300 K

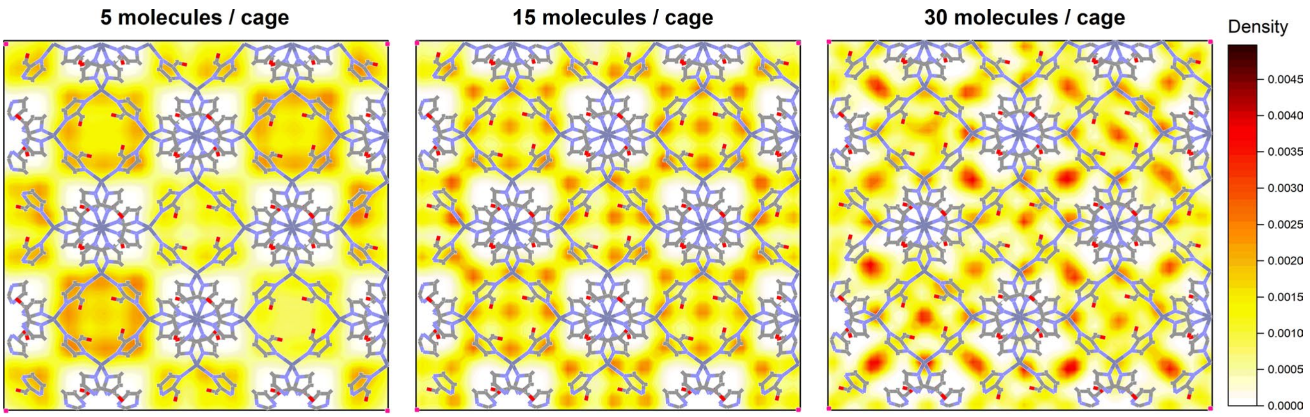


Fig. 7 Density plots of CO_2 in the *x*–*y* plane of the last 0.5 ns, 300 K at loading of 5, 15, and 30 molecules/cage

cage, six-membered ring window diameter is changed from 3.55 to 4.34 Å at 300 K, respectively. Particularly, the transition state is captured at 25 molecules per cage. However, the increase in temperature from 100 to 473 K can adjust the window diameter quickly. Finally, it can be concluded that not only the number of CO_2 molecules but also temperatures can induce the gate-opening effect.

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Temperature and Gas Loading Induced Structural-Dynamics Properties of Zeolitic Imidazolate Framework-90

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ABSTRACT

The effects of temperature and number of gas molecules in ZIF-90 were studied by using Gibbs Ensemble Monte Carlo (GEMC) simulations and Molecular Dynamics (MD) simulations. The adsorption and diffusion coefficients resulting from single gases, H_2, CH_4 and CO_2, and H_2/CH_4 mixture are expected to yield information *i.e.* structural and dynamics properties. In this work we found the optimal parameter set between gas molecules and ZIF-90 framework as proved by adsorption isotherm calculations when compared with experimental data. Interestingly, the structural change namely gate opening in ZIF-90 appeared only at high temperatures under loading with H_2, CH_4 molecules and H_2/CH_4 mixture. For CO_2 molecules, the gate opening appeared caused by both temperature and number of CO_2 molecules loading as well. The preferential adsorption site for all gas molecules is located at the organic linker of ZIF-90. The diffusion coefficient shows high mobility at high temperature while adsorption in ZIF-90 is low for all gas molecules at high temperature. Also an increase of the membrane selectivity by increased temperature could be found for H_2/CH_4 mixture.

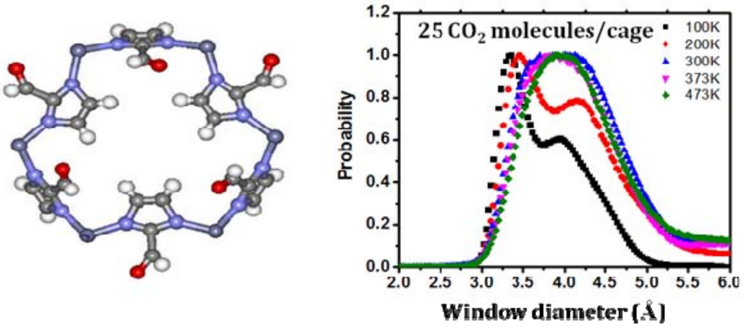

Figure1. The window diameters of ZIF-90 when loading 25 CO_2 molecules/cage.

Keywords: Gate Opening, Adsorption, Diffusion, ZIF-90, MD and GEMC Simulations

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The Effect of Temperature and CO_2 Loading on Structural and Dynamics Properties of Zeolitic Imidazolate Framework

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Abstract:

Several new classes of porous materials have been developed recently. Particularly, Zeolitic Imidazolate Frameworks (ZIFs) came into the focus of interest because of their great diversity, the big pores and the possibility of custom-made design. In this work, the effects of temperature and number of gas molecules in ZIF-90 were investigative by using Gibbs Ensemble Monte Carlo (GEMC) simulations and Molecular Dynamics (MD) simulations. The adsorption and diffusion coefficients resulting from single gases, H_2, CH_4 and CO_2, and H_2/CH_4 mixture are expected to yield information *i.e.* structural and dynamics properties. The optimal parameter set between gas molecules and ZIF-90 framework as demonstrated by adsorption isotherm calculations when compared with experimental data. Fascinatingly, the structural change namely gate opening in ZIF-90 appeared only at high temperatures under loading with H_2, CH_4 molecules and H_2/CH_4 mixture. For CO_2 molecules, the gate opening appeared caused by both temperature and number of CO_2 molecules loading as well. The preferential adsorption site for all gas molecules is detected at the organic linker of ZIF-90. The diffusion coefficient illustrations high mobility at high temperature whereas adsorption in ZIF-90 is low for all gas molecules at high temperature. Moreover, an increase of the membrane selectivity by increased temperature could be found for H_2/CH_4 mixture.

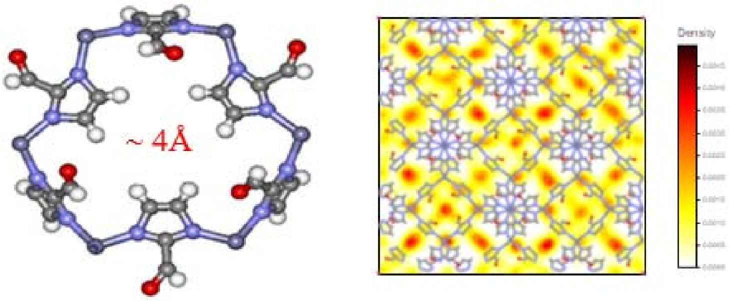

Figure1. The window diameters and density plot of ZIF-90 when loading 25 CO_2 molecules/cage.

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Keywords: Adsorption, Diffusion, Zeolitic Imidazolate Frameworks (ZIFs), Molecular Dynamic Simulations and Gibbs Monte Carlo Simulations

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ABSTRACTS

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have been linked to the rates of microscopic processes governing the polymerization. The understanding thus obtained has been used to draw comparison with the experiments. Further, study of the structure of the filaments reveals that beyond a threshold value of hydrophobic interactions among the achiral building blocks, there is a transition to helical structure.

Extraordinary adsorption/reaction selectivity of NO_x from N_2 by combined adsorption and reaction on MIL-127 (P)

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For the first time the strong enhancement effect of the recombination reaction $N_2O_4 \leftrightarrow 2\ NO_2$ (see, e.g., I. Matito-Martos *et al.*, Phys. Chem. Chem. Phys. 20 (2018) 4189) inside the restricted geometry of the Metal-Organic-Framework (MOF) MIL-127 is used for the separation of NO_2 and N_2O_4 from N_2 (air). The number of N atoms in the nitrogen oxides NO_x and that in N_2 is used to define a selectivity of the combined adsorption and chemical reaction process that can reach values of about 1000. This result is obtained from extensive computer simulations. The equilibrium between a gas phase in simulation box A and molecules adsorbed in MIL-127 in simulation box B has been examined by Gibbs Ensemble Monte Carlo simulations (GEMC) employing the home-made software "Gibbon". The chemical reaction equilibrium between NO_2 and N_2O_4 has been treated by simulations using RxMC, a special version of Monte Carlo simulations. The basic idea of RxMC is that the chemical equilibrium (like usual equilibrium without chemical reaction) can be described by the grand canonical partition function. In the classical version of the grand canonical partition function its integrand is the probability density of the possible states of the system. Thus a Monte Carlo random walk using this probability density can be carried out.

Tuning interaction in long-range models changes dynamical scaling during aging

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The understanding of the aging phenomenon, even though being manifested for a range of nonequilibrium processes, is still predominantly limited to short-range systems. To bridge this gap we, here, via Monte Carlo simulations, explore aging during coarsening of the power-law interacting long-range Ising model in two spatial dimensions. We show that the dynamical scaling of the spin-spin two-time autocorrelation function is best described via sub-aging in the long-range regime $\sigma \leq 1$ with the sub-aging exponent μ depending on the power-law exponent σ of the model. In the effectively short-range regime $\sigma > 1$ we recover the simple aging behavior. From our analyses, we also conjecture that the autocorrelation decay exponent $\lambda = \sigma$ in the long-range and $\lambda = 1.25$ in the short-range regime.

[1] H. Christiansen, S. Majumder, M. Henkel, and W. Janke, preprint `arXiv:1906.11815` (2019).

Molecular Simulation on Gate-Opening Phenomena in ZIF-90 Induced by CO_2

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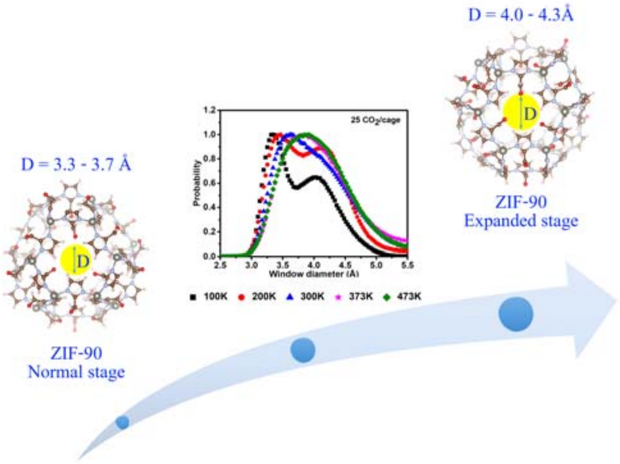
A new subclass of MOFs which has zeolitic structure are called zeolitic imidazolate frameworks (ZIFs). The lattice flexibility of these materials is a key factor in many applications. One of the physical phenomena in flexible porous materials is gate-opening that dependents on many factors such as species of the adsorbed molecules, amount of adsorbed molecules, pressure and/or temperature. The investigation of gate-opening of several ZIFs can provide better understanding of adsorption and diffusion. These outcomes have impact on performance of ZIFs in the industrial separation process. The aim of this work is to investigate the gate-opening in ZIF-90 as a function of the number of CO_2 and the temperature using molecular simulation. The influence of adsorbed CO_2 molecules on the lattice structure of ZIF-90 has been examined. Two structures corresponding to so called gate opening can be observed depending upon the amount of adsorbed guest molecules and the temperature. A transition region has been found in which both of the structures appear temporarily leading to broad statistical distributions of window diameters. Diameters up to 4.43 Å are found. An increased window diameter is observed at high temperature even for the empty lattice.



Keywords: ZIF-90; Gate opening effect; Carbon dioxide; Molecular simulation