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

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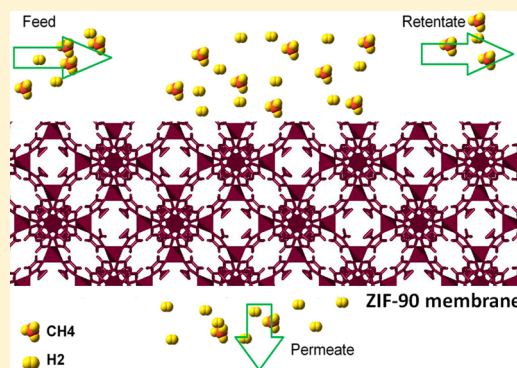
1. INTRODUCTION

With a narrow window size of about 3.5 Å and exceptional thermal and chemical stability, the metal−organic framework (MOF) zeolitic imidazolate framework (ZIF) of structure type ZIF-90[1] is proposed as a promising candidate for a gas separation material. In the ZIF-90 structure, zinc ions are interconnected by imidazole-2-carboxyaldehyde linker molecules forming a sodalite (SOD) framework structure. Among the gas mixtures to be separated, hydrogen (H_2) is of special interest, e.g., as a future fuel in a PEM fuel cell or for catalytic hydrodesulfurization of natural gas or refined petroleum products. Hence, the process of hydrogen separation from mixtures, e.g., the H_2/CH_4 mixture, is highly interesting. In 2010, Huang et al.[2] used ZIF-90 as a membrane for hydrogen purification with the expectation of a high separation factor due to the different diameters of H_2 (2.9 Å) in comparison with other larger gases like CH_4, CO_2, and N_2 (3.3−3.8 Å).

However, the selectivity values from mixed gas permeation experiment are lower than the ideal separation factors predicted from single gas permeation studies. This experimental finding is attributed to the flexibility of the lattice so that guest molecules with kinetic diameters larger than the window size are able to enter the MOF framework, thus passing the membrane.[2−7] In addition to this, heating the ZIF membrane up to 200 or 225 °C could surprisingly increase the effectiveness of the separation on this membrane.[2,4−6] Therefore, a theoretical study of molecular adsorption and diffusion at different temperatures is desirable to obtain deeper understanding of these processes on the atomic scale.

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

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

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

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

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

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

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

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

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

2. SIMULATION DETAILS

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

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

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

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

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

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

Also, the partial charges have been treated as described in detail in ref 7. In this method, all the Coulomb potentials of the partial charges of each individual neutral molecule are treated together as a sum, leading to a fast decay of this sum at large distances. Cutoff effects, caused by the slightly different positions of the partial charges within one molecule, are avoided. This method resembles the method for charge groups proposed in ref 21.
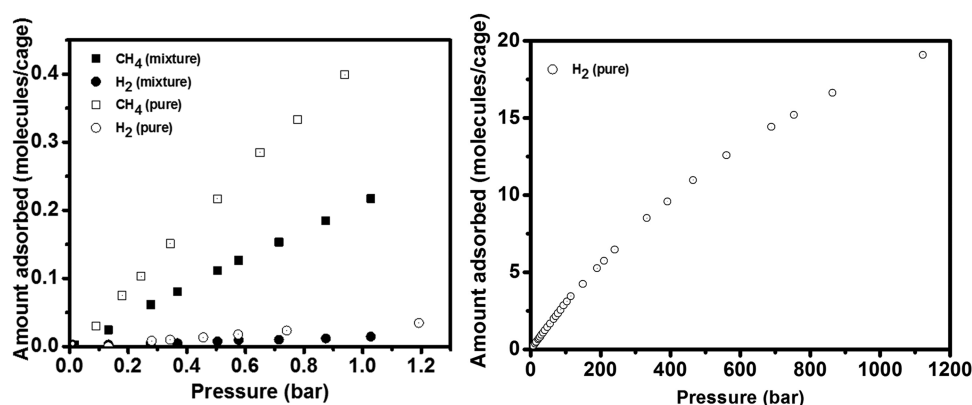
Figure 1. Adsorption isotherms of the single components CH_4 and H_2 as well as of the equimolar H_2/CH_4 mixture in ZIF-90 at 300 K (left-hand side) and the adsorption isotherm of pure H_2 at 300 K up to 1122 bar (right-hand side). Note that the abscissa data give, in the case of the mixture, the total pressure as sum of the partial pressures.
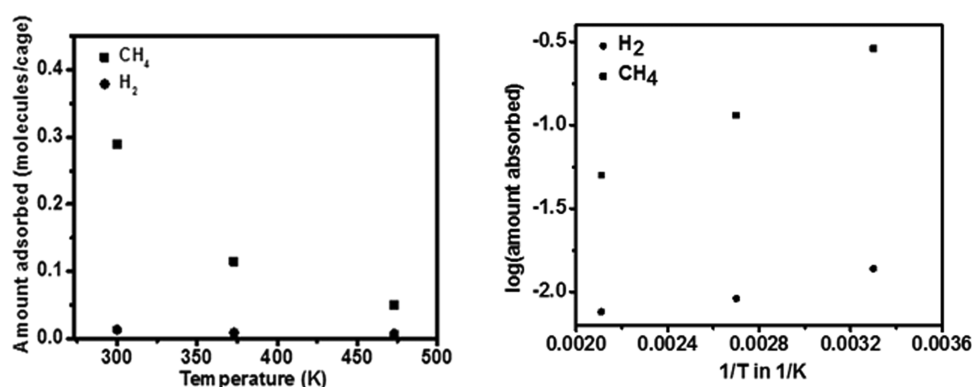

Figure 2. Left: Adsorbed amounts of CH_4 and H_2 as a function of temperature at 1 bar total pressure of the equimolar gas mixture H_2/CH_4. Right: The same as an Arrhenius plot.

3. RESULTS AND DISCUSSION

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\langle N \rangle = \beta V_{\text{eff}} p \tag{4}$$

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

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

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

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

3.2. Diffusion. The self-diffusion coefficient D_s of the guest molecules has been calculated at 3 different temperatures corresponding to the experiment and is shown in Figures 3 and
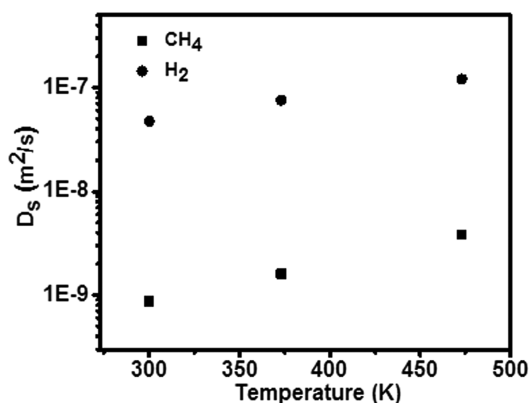

Figure 3. D_s of CH_4 and H_2 in H_2/CH_4 mixture at different temperatures at a very low loading (0.25 CH_4 + 0.25 H_2 molecules/cage) in ZIF-90.

4. Unfortunately, the diffusion calculations for H_2 could not be done in the mixture that is adsorbed from the equimolar gas mixture because the number of adsorbed H_2 molecules is too small to calculate D_s with satisfactory accuracy. However, at low pressure there is minimal interaction between the diffusing molecules, and they should diffuse independently of each other. Hence, we perform the MD simulations as equimolar in the ZIF, and we assume that the D_s of hydrogen obtained in this way at quite low loading can be used also as an approximate value for the lower loadings. Additionally, we check the loading
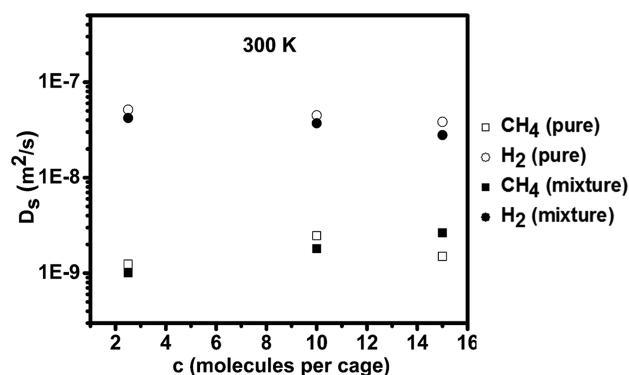

Figure 4. D_s at three different loadings for the pure components CH_4 and H_2 as well as the equimolar adsorbed H_2/CH_4 mixture at 300 K. This is to say, in the case of the mixture, from 8 molecules per cage, 4 CH_4 and 4 H_2.

dependence of the D_s at higher pressure where it can be obtained from MD more easily.

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

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

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

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

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

Remarkably, the self-diffusion coefficients D_s's for the pure single component adsorbate and for the adsorbed mixture are not very different from each other if the total amount of adsorbed molecules is the same even for loadings up to 15
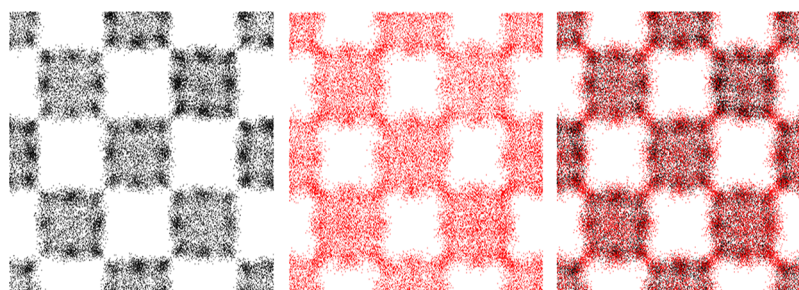
Figure 5. Density distributions of the two kinds of guest molecules at 300 K for 5 CH$_4$ + 5 H$_2$ molecules per cage. Red: hydrogen. Black: methane. The picture on the right shows the combination of the two others.
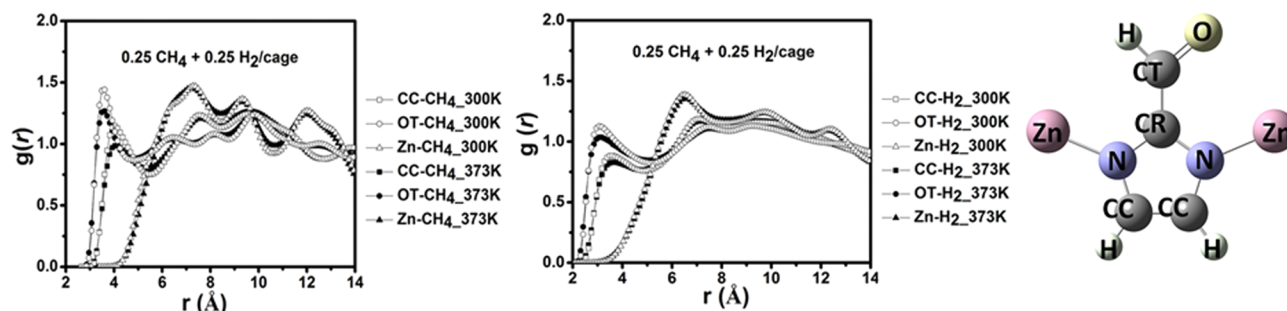

Figure 6. RDFs of the CH$_4$ and H$_2$ with selected atoms in ZIF-90 at 300 and 373 K at the low guest molecule concentration of 0.25 CH$_4$ + 0.25 H$_2$/cage and organic linker.

molecules per cage. For example, the D_s of H$_2$ is only slightly smaller if half of the H$_2$ molecules are replaced by the heavier CH$_4$ molecules. At high loading, the D_s of CH$_4$ is somewhat larger in the mixture when half of the CH$_4$ molecules have been replaced by the lighter H$_2$. If this is true even at higher loadings, then this finding strongly supports the assumption that the D_s in the low pressure region (1 bar as in ref 2) does not depend on the concentration ratio of the mixture. Thus, the results of our adsorption and diffusion studies, which we need for the calculation of permeation selectivities, can be extended to nonequimolar feed mixtures.

Probability densities of particle locations for the adsorbed H$_2$/CH$_4$ mixture are plotted in Figure 5. The red dots refer to the sites of H$_2$, and the green dots represent the sites of CH$_4$ in snapshots taken every 100 steps from the last 50 000 steps in MD simulations to describe the position probability of methane and hydrogen during simulation time.

It can be seen that, at this quite high density, both kinds of molecules are distributed over the whole cavity. The overlay shows that some H$_2$ molecules reside closer to the cavity walls than any CH$_4$ molecule. However, this is probably only due to the smaller diameter of H$_2$.

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

At low adsorbate density, favorite adsorption sites of both CH$_4$ and H$_2$ are the oxygen atoms of the aldehyde group of the linker in the ZIF-90 lattice. Other sites of high probability are CC, which means the organic linker is in agreement with many other ZIFs and with the single gas CH$_4$ in ZIF-90 in the previous work.[13−15,23−26]

3.3. Comparison of our MD Calculations with Permeation Experiments.
For a comparison of the results with the experiment, the permeability is calculated from the

adsorption and diffusion data by the following equation. The results are shown in Figure 8.

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

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

In Figure 7, the simulation results of this work are shown for the permeance, with a rather good agreement with the experiment.[2] While the permeance of H$_2$ agrees quite well with the experiment, the permeance of CH$_4$ is slightly overestimated. Atci's work,[8] which uses a rigid framework
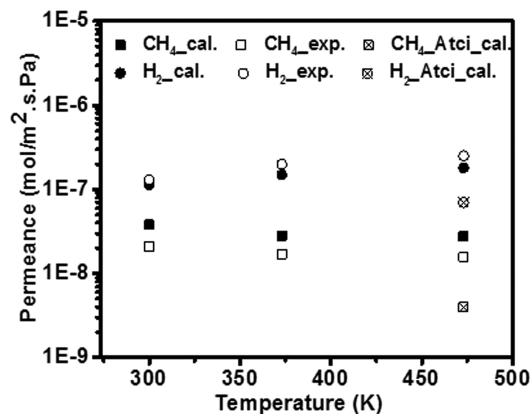

Figure 7. Comparison of the calculated membrane permeances for the equimolar H$_2$/CH$_4$ mixture in comparison with the permeation experiment[2] and Atci's work.[8]

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Figure 9 shows that, in contrast to the window size, the total size of the simulation box and hence also the lattice does not
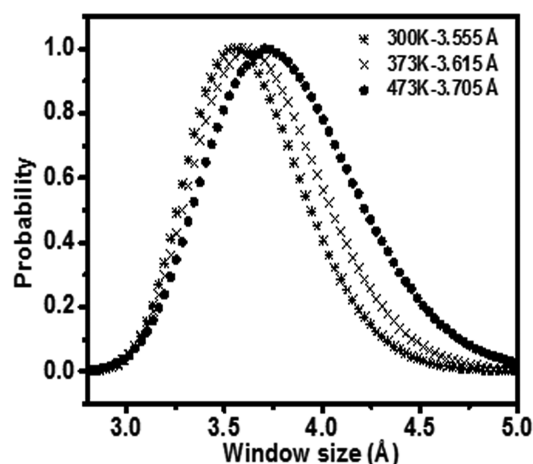

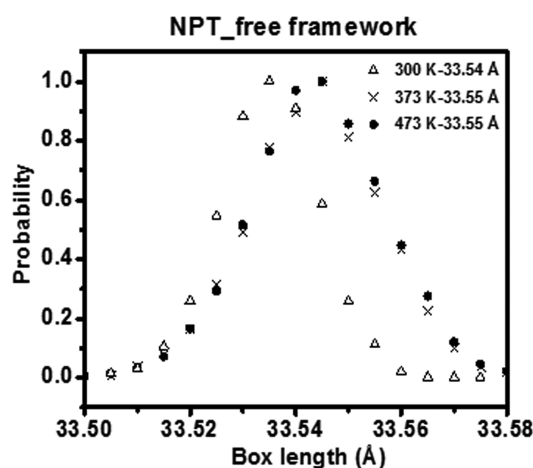**Figure 8.** Probability distributions of the window size.

Figure 9. Probability distribution of box length.

change significantly with the increase of the temperature in the NPT simulation. In detail that means that the box length has a positive expansion but with a very small percentage (around 0.03%). This is also in agreement with the types of ZIFs which have SOD topology.[17]

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

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

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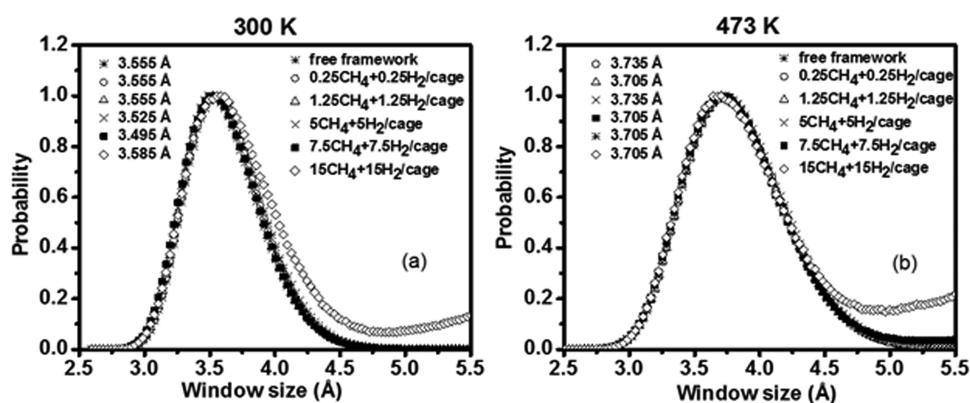
Figure 10. Probability distribution of the window size in two different temperatures: (a) 300 K and (b) 473 K.

4. CONCLUSIONS

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

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

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

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

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

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

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Notes

The authors declare no competing financial interest.

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