Adsorption And Diffusion of The $H_2/CO_2/CO$ /MeOH /EtOH Mixture Into The ZIF-7 Using Molecular simulation

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Abstract

The adsorption and diffusion of synthesis gas components (methanol, ethanol, H_2 , CO_2 , and CO molecules) in ZIF-7 by grand canonical Monte Carlo and molecular dynamics simulation were investigated. The initial diffusion coefficient at the beginning of the process depends on the kinetic diameter of the guest molecules. Also, the diffusion coefficient at equilibrium conditions probably depends on the interaction between the guest molecules with the ZIF-7 framework. The radial distribution function results indicate that the distribution of guest molecules in the framework is affected by the interaction between the guest molecules. These results also demonstrate that the Zn atom and the organic linker are favorable sites for CO_2 , CO, and H_2 . In contrast, the organic linker is the most favorable adsorption site for methanol and ethanol guest molecules. In addition, the diffusion coefficient of guest molecules in binary mixtures is related to the attraction or repulsion between the guest molecules.

Introduction

In the petrochemical industry, methanol (MeOH) is one of the most important industrial chemicals that serve as both a renewable fuel and an intermediate for the production of many chemicals [1–4]. In the industrial process, MeOH is produced from CO, CO_2 , and H_2 gas mixture (synthesis gas) by heterogeneous catalysts [2, 5–10]. The MeOH purification from unconverted synthesis gas and ethanol (EtOH) is a more difficult and complex process, which is used using appropriate membranes [8, 9]. The separation of MeOH and EtOH as process products from reactants is of very importance to increase the efficiency of synthetic gas production units. To achieve a suitable separation, various adsorbents such as inorganic adsorbents for example Pd-based metal adsorbents, microporous silica adsorbents, carbon adsorbents, and zeolite adsorbents [3, 4, 9, 11–13], and Metal-organic frameworks (MOFs) [14–16] are used in syngas purification.

Metal-organic frameworks (MOFs) are a new class of nanoporous materials, which are composed of transition-metal centers and organic linkers with unique characteristics such as large pore volume, low density, and high surface areas [17–22]. The MOFs due to various topologies have different applications such as gas storage and separation [14–16, 23–25], catalysis [21, 26–30], luminescence [31], biomedicine [32], and sensors [33]. A new and interesting class of MOFs is zeolitic imidazolate frameworks (ZIFs) which have chemical and thermal stability and share similar pore topologies with zeolites [22, 34, 35]. The ZIFs structures are composed of tetrahedral units formed by one bivalent metal M^{2+} ions and four imidazolate anions (Im^-), similar to the SiO_2 tetrahedra in zeolites [34, 36, 37]. In other words, the framework unit of M-Im-M is similar to that of Si-O-Si in zeolite, where Si and O atoms are replaced by metal ions and Im, respectively [38, 39].

Currently, many studies have been conducted for alcohol, CO_2 , and light molecules adsorption and diffusion in ZIF frameworks. Hertäg et al. have investigated the diffusion of CH_4 and H_2 with flexible ZIF-8 models using molecular dynamics simulations and several sets of force field parameters [40]. They have reported that flexibility is an important factor to describe the diffusion of methane in ZIF-8. Bergh

and Gucuyener have studied the adsorption of ethane and ethylene in ZIF-7 and found that it preferably absorbs ethane rather than ethylene [41, 42]. Zhang et al. have explored the adsorption of $C_1 - C_4$ alcohols in the ZIF-8 and reported that the interaction between alcohol and the ZIF-8 framework enhanced as the chain length of alcohol increased [6]. Battisti et al. simulated the adsorption and dynamics of CO_2 , CH_4 , N_2 , H_2 , and binary mixtures in the ZIF-2 to ZIF-10. They reported that ZIF-5, ZIF-7, and ZIF-9 fulfill the condition for molecular sieving separation of H_2 [10]. Liu et al reported that ZIF-7 is a prospective material in hydrogen adsorption and separation[43].

In this study, ZIF-7 was simulated to study adsorption and diffusion of H_2 , CO, CO_2 , MeOH, and EtOH guest molecules which has been rarely studied in previous works. The calculated adsorption isotherms for the guest molecules were compared, and the adsorption mechanism was evaluated from a microscopic level. In addition, the effects of the presence of guest molecules and framework on guest molecule adsorption in ZIF-7 were evaluated.

Simulation Details

In this work, adsorption, and diffusion of CO_2 , CO, H_2 , MeOH, and EtOH in the ZIF-7 framework were investigated. This structure is formed by zinc as metal centers connected by imidazole linkers. For the description of the gas-adsorbent interaction, the UFF force field was used that its potentials were successfully used in a wide range of organic frameworks such as ZIFs [44–49]. All the simulations were performed using the Accelrys Materials Studio simulation software [50].

2.1. Adsorption method

Grand canonical Monte Carlo (GCMC) and the Metropolis method with periodic boundary conditions were applied to simulate the adsorption [50–52]. The GCMC method has been used to simulate the adsorption behavior of the gas mixtures [6].

The Ewald summation method and atom-based with an accuracy of 0.0001 kcal/mol were used to describe the electrostatic and van der Waals interactions, respectively. The size of the simulation box was $22.98 \times 22.98 \times 15.76 \text{ \AA}^3$ and the integration time step was 1fs. The number of equilibration steps to be carried out before the production stage includes 2500000 steps and the same number for the production stage was used. The charges are applied using the QEq method. Adsorption behavior was investigated in the pressure range of 1 to 10,000 kPa

2.2. Diffusion method

To investigate the diffusion behavior the system was initially equilibrated at 200.0 ps and followed by 1500 ps NVT-MD simulations [53–55]. The velocity Verlet algorithm was used to integrate the equations of motion [53]. To regulate the temperature (at 300 K) the Nose thermostat was used [53]. The configurations were saved every 1000 steps.

.The self-diffusion coefficient (D_s) values of components within the ZIF-7 framework were calculated using the mean squared displacement (MSD) according to the Einstein relation [56, 57]:

$$D_s = \lim_{t \rightarrow \infty} \frac{1}{6t} \left\langle \frac{1}{N} \sum_{i=1}^N |r_i(t) - r_i(0)|^2 \right\rangle \quad (1)$$

where $r_i(t)$ is the position vector of guest molecule i at time t and N is the number of diffusive atoms in the system. To estimate the electron density difference between the zinc atoms and the linker, the density functional theory (DFT) computation was carried out using the B3LYP functional [58]. The plane-wave basis set energy cutoff was set at 500eV.

Results And Discussion

3.1. ZIF-7 structure

ZIF-7 includes zinc atoms connected by benzimidazolate (blm) linkers in tetrahedral coordination (Fig. 1). As shown in Fig. 1, the sodalite (SOD) cages, which are connected via three types of small apertures in the ZIF-7 framework, include one four-member ring-type pore, two types of six-member ring pores. Type A six-member-ring pore (pore A) has a larger void space than type B (pore B) in the ZIF-7 framework. The position of the benzene rings in the optimized structure in a vacuum narrows the pore entrance to about 0.3 nm [41]. The crystal structure of ZIF-7 before guest adsorption is rhombohedral with the space group R-3 and unit cell parameters as, $a = b = 22.98 \text{ \AA}$ and $c = 15.76 \text{ \AA}$, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$. The experimentally determined unit cell structure ZIF-7 was taken from the Crystallography Open Database (COD) [59]. After adsorption, the framework is changed to triclinic with the space group P-1 and unit cell parameters as, $a = 23.95 \text{ \AA}$, $b = 21.35 \text{ \AA}$ and $c = 16.35 \text{ \AA}$, $\alpha = 90.28^\circ$, $\beta = 93.28^\circ$ and $\gamma = 108.41^\circ$ which is exactly following experimental crystallographic data [59]. The guest molecules can pass through the pores and adsorb onto the SOD cage surface.

In addition to the pore structure of ZIF-7, the electrostatic potential (EP) pattern of the framework is used for interpreting and predicting the reactivity of the guest molecules [60, 61]. The electrostatic forces between an adsorbent structure and guest molecules would mainly affect the guest molecule incoming and moving within the ZIF-7 framework. Thus, the analysis of the EP property of the ZIF-7 structure can facilitate the diffusion of guest molecules within the framework [62]. Figure 2 shows the EP distribution of zinc atoms connected by blm linker, which identifies the electrophilic or nucleophilic centers.

3.2. Pure guest molecule adsorption and diffusion

The density of CO, CO₂, EtOH, MeOH, and H₂ guest molecules in ZIF-7 is shown in Fig. 3. According to Fig. 3, CO, CO₂, and MeOH adsorption initially takes place in pore B at low pressure and migrates from pore B to pore A at high pressure. These results show that the path of entry of these guest molecules from six-member-ring pore B is more suitable than pore A. After accumulating these guest molecules in pore B, they migrate from pore B to pore A, which provides a larger space for guest molecules. This migration

takes place through the rotation of linkers connected to these two types of pores, which changes the structure of ZIF-7 from rhombohedral to triclinic. Zhao et al.'s results show that the CO₂ molecules migrate from pore B to pore A via the rotation of linkers [63]. But the adsorption behaviors of EtOH and H₂ molecules are different and at the beginning of adsorption and high pressure are equally distributed in these two pores. This result shows that blm linkers in the ZIF-7 framework are favorable adsorption sites for MeOH and EtOH guest molecules, but the Zn clusters are the appropriate adsorption sites for CO, CO₂, and H₂ guest molecules.

The diffusion coefficients of guest molecules in the ZIF-7 framework were calculated from the slope of mean squared displacement (MSD) analysis of single guest molecules trajectories in Fig. 4. As shown in Fig. 4, the MSD curves initially exhibit a sharp increase with time and follow a slow increase which indicates the guest molecules have two-stage diffusion. At the initiative of the adsorption process, the guest molecules have a fast diffusion but decrease over time. Therefore, two types of diffusion coefficients can be calculated for the initial of the diffusion process (D_{SI}) and when the diffusion process reaches equilibrium (D_{SE}). These results calculated from MSD values are listed in Table 1. Fast and slow diffusions are dominated by intra-cage and inter-cage mobility of guest molecules, respectively [64]. At the beginning of the diffusion process, the calculated diffusion coefficient of the studied guest molecules is in the order of $D_{H_2} > D_{MeOH} > D_{CO} > D_{CO_2} > D_{EtOH}$. This result shows that the diffusion coefficient (D_{SI}) at the beginning of the process may depend on the kinetic diameter of the guest molecules (Table 1) and the interaction between guest molecules and the gate of pore structures. But the diffusion coefficient at equilibrium conditions (D_{SE}) probably depends on the kinetic diameter of the guest molecules and how the guest molecule interacts with the ZIF-7 structure. At the equilibrium, the calculated diffusion coefficient of the studied guest molecules is in the order of $D_{H_2} > D_{MeOH} > D_{CO_2} > D_{CO} > D_{EtOH}$. The fast diffusion of H₂ can be attributed to the small size of H₂.

Table 1
Kinetic Diameter, Dipole Moment, and the calculated diffusion coefficient of the guest molecules at the beginning of the diffusion process (D_{SI}) and diffusion coefficient at equilibrium conditions (D_{SE}).

Guest molecule	Kinetic Diameter (Å)	Dipole Moment (D)	D_{SI} ($\times 10^{-10}$ m ² /s)	D_{SE} ($\times 10^{-10}$ m ² /s)
H ₂	2.9	0	21.0	0.090
CO ₂	3.3	0	8.7	0.013
CO	3.8	0.12	9.0	0.008
EtOH	4.5	1.44	3.3	0.007
MeOH	3.6	1.71	10.8	0.015

The ZIF-7 crystals are formed by the attack of un-conjugated lone pairs of neutral blm linkers to the partially positive terminal zinc atoms as electrophilic sites to keep the charge-balanced. As shown in Fig. 2, the terminal Im linker introduces ($-N-H$) functionality to the structure as nucleophilic sites in the ZIF-7 framework. These electrophilic or nucleophilic sites caused to dipolar interaction with MeOH and EtOH guest molecules with high dipole moment (Table 1) and the higher diffusion of MeOH than CO_2 with the same kinetic diameter may be related to the higher dipole moment of MeOH.

The radial distribution function (RDF) is used to evaluate the presence of guest molecules around adsorption sites in the ZIF-7 framework. Figure 5 shows the label of the atoms present in the ZIF-7 structure as well as RDF ($g(r)$) results of the guest molecules as a function of distance (r). As shown, the guest molecule density shows two peaks around C_1 and C_2 atoms at $r \approx 3.5$ Å, with a higher density around C_1 atoms of the organic linker. The higher density of guest molecules around the C_1 atom is probably due to the lower spatial barrier of the ZIF-7 structure at this position. This result indicates that around the C_1 atoms is more space for the accumulation of absorption guest molecules. The board peaks around C_1 and C_2 atoms indicate the displacement of molecules around these absorption positions. The smaller peak at around $r = 4.0$ Å is related to guest molecules around C_3 atoms, which shows that this position is less favorable for studied guest molecules. The $g(r)$ around Zn atoms displays distinct peaks at short distance $r = 5$ Å and long-distances $r = 9$ Å, respectively, which are very strong for CO, CO_2 , and H_2 guest molecules. Thus, the preferred adsorption sites for CO, CO_2 , and H_2 guest molecules are the atoms of the organic linker (especially C_1 atom). Although, the Zn atoms also can be are favorable adsorption sites for CO, CO_2 , and H_2 . Perez-Pellitero et al reported that the preferential adsorption sites for CO_2 adsorption in ZIF-8 are the organic linkers [65]. For EtOH guest molecules the first peak is seen at a distance of 2.2 Å from the N, C_3 , C_4 , and Zn atoms. Although the intensity of these peaks is not high, their thinness indicates that the ethanol molecules are not able to displace around these absorption positions. This distance probably indicates a hydrogen-type interaction between the hydrogen atom of the ethanol hydroxyl group and the unbonded electron pair of the N atom. EtOH, with its chain-like state, has been able to adjust its position so that its hydrogen atom is available to the N, C_3 , C_4 , and Zn atoms. Thus the preferred adsorption site for EtOH is the N atoms, and the organic linker in ZIF-7 is the most favorable adsorption site for MeOH and EtOH guest molecules, rather than the metal cluster. A similar result was observed in Zhang et al.'s results for MeOH adsorption in ZIF-8[6].

Figure 6 shows the adsorption isotherm of guest molecules at 300 K. Since the adsorption results of the simulation are reported in terms of molecule/UC (i.e. unit cell), to compare the equilibrium guest molecule capacity with experimental results, it is necessary to convert this term to mol/kg. Eq. 2 was used for this conversion [66]:

$$q \text{ (mol/kg)} = q \text{ (molecule/UC)} / \rho V N_{Av} \text{ (2)}$$

That N_{Av} is the Avogadro constant, ρ and V are density and volume, respectively which in this study equal 1.24g/cm^3 and 7214 Å^3 .

As shown in Fig. 6, the loading of EtOH and MeOH is more than other components at low pressure, and the loading of CO and H₂ increased dramatically by adsorption pressure. Considerable loading of EtOH and MeOH at low pressure is related to higher dipolar interaction with the ZIF-7 framework. However, the saturation loading of MeOH (17.8 molecule/ UC) or (3.58 mmol/g) is more than that of EtOH (12 molecule/ UC) or (2.23 mmol/g), due to the smaller size of MeOH molecules. Also, higher interaction of EtOH guest molecules with linkers and lower interaction with Zn atoms makes the EtOH guest molecules less concerned to accumulate in the cage cavity of the ZIF-7 structure, so the loading does not increase with increasing pressure (Fig. 3). The results show that the H₂ loading at appropriate pressures in this work does not reach saturation, which may be related to the small size of the H₂ molecules. Figure 6 shows the CO loading at low pressure is fewer and at high pressure is higher than other guest molecules, due to different interactions with the ZIF framework. As the inter surface of the ZIF-7 framework is hydrophobic [62, 67, 68], the CO guest molecules at low pressure cannot diffuse in the inner network. With the rising of the system pressure the cage-filling occurs in the SOD cage of the ZIF-7 framework and at high pressure, the whole sodalite cage is about filled. At high pressure, the CO guest molecule can diffuse in a hydrophobic pore structure thus the CO loading shows the highest loading [67, 69].

Figure 7 shows the adsorption Q_{st} of guest molecules (Q_{st}) as a function of pressure at 300 K. The Q_{st} of adsorption is an important parameter for guest molecule loading at low pressure and higher Q_{st} cased to more loading at this condition. According to Fig. 7, the Q_{st} trend is EtOH > MeOH > CO₂ > CO > H₂. Thus higher loading of EtOH at low pressure may be related to higher Q_{st}, due to the more strongly interaction of EtOH with the ZIF-7 framework [70]. According to Fig. 5, EtOH has a long and relatively sharp peak around the nitrogen atom, indicating a strong hydrogen bond interaction that results in high Q_{st}. A similar result has been reported by Zhang et al.[6] and Mosier et al.[67]. As shown in Fig. 7, the calculated Q_{st} of adsorptions for guest molecules is dependent on the pressure. According to Fig. 7, the Q_{st} of EtOH adsorption initially is almost independent of pressure, which is attributed to the homogeneity of ZIF-8 to ethanol adsorption. Then, the Q_{st} value rises with EtOH pressure, which corresponds to increasing loading region (~ 15.8 kPa, Fig. 6) and with passing through a maximum drop and becomes nearly constant finally. Zhang et al. reported a similar result for EtOH adsorption in ZIF-8 [68]. Two types of interactions are effective on the Q_{st} value, one of them is adsorbate-adsorbent interaction and the other is the adsorbate-adsorbate interaction [71]. The increasing trend of Q_{st} with increasing EtOH loading is ascribed to the cooperative attraction between EtOH molecules and the occupation of the more favorable adsorption sites. However, the increasing EtOH loading leading to a weaker interaction of EtOH with the ZIF-7 framework due to the occupation of the less favorable adsorption sites, and also the interaction between EtOH molecules become less attractive due to steric constraint. Therefore Q_{st} drops at high loading, where EtOH adsorption is saturated. In the case of MeOH and CO guest molecules, also this explanation can be used. There are two broad peaks in Q_{st} of MeOH, which occurs at 15.8 and 251 kPa corresponding to loading of 13.3 and 15.4 molecule/UC, respectively in the isotherms (Fig. 6). Since, MeOH guest molecules are not saturated at studied pressures, Q_{st} of MeOH increases after the second peak. There is one broad peak in Q_{st} of CO, which located between 6.3 and 631 kPa corresponding to the loading of 0.3 and 3.9 molecule/UC in the isotherm (Fig. 6).

The CO₂ adsorption isotherm in Fig. 6, exhibits a general trend of monotonic and smooth increase, a similar result is found in Long et al.[72] and Du et al. [73] studies. Initially, the less adsorption of CO₂ guest molecules in Fig. 6 is attributed to the weak binding of these molecules with pore B [63]. With increasing loading and aggregation of CO₂ molecules in pore B, the rotation of shared linker between pores B and A occurs leading to CO₂ flowing from pore B into pore A [63]. Subsequently, the increase in CO₂ adsorption capacity is confirmed by Fig. 3.

The calculated Q_{st} of CO₂ adsorption up to 39.8 kPa equals 9.4–9.3 kcal/mol (~ 39.3–39 kJ/mol), which is almost independent of loading. Then, it decreased to 8.6 kcal/mol (~ 36 kJ/mol), which following Du et al. results for CO₂ adsorption in ZIF-7 [73]. The equilibrium CO₂ capacity, q, according to the Fig. 6 is 10 molecules/UC (2.2 mmol/g), which is equal to Yang et al. [74] and Rahman et al. [75] results.

3.3. Mixed guest molecules interactions

In this section, the effects of mixed guest molecules on their interactions with ZIF-7 are investigated. For this purpose, the guest molecules were placed together in the ZIF-7 framework and the interactions were evaluated from RDF results. Figure 8 shows the RDF results for guest molecules in the mixture (29%CO, 3%CO₂, 58%H₂, 8%MeOH, 2%EtOH) as a function of distance (R) with the ZIF-7 framework. As shown in this figure, the RDF pattern of guest molecules within the structure in the mixed state with their single state (Fig. 5) is reasonably different. As shown, the guest molecules density shows two peaks around C₁ and C₂ atoms at r = 3.5 Å, with higher density around C₁ atoms of organic linkers. In comparison to the RDF results with single guest molecules (Fig. 5), the presence of guest molecules in a mixture around C₁ atoms decreased. The CO guest molecule has a strong interaction with C₁ at 3.39 Å, which has shifted to a shorter position than the pure state. Also, its interaction with C₃ is stronger (compared to pure), but the peak of the zinc atom is weakened. For the CO₂ guest molecule in the mixture, the interactions are increased through C₄, N, and zinc atoms. Also, the CO₂ guest molecule in the mixture guest molecules has a more uniform distribution in the ZIF-7 framework than in the single CO₂ guest molecule. RDF results in Fig. 8 show that the interaction of MeOH with both Linker and the zinc atom becomes stronger in the mixture. These results show that the presence of H₂ guest molecules around the C₃ atom in the mixture has increased, which is related to the small size of this molecule compared to others. Also, RDF results in Fig. 8 show that the interaction of H₂ with both Linker and the zinc atom becomes stronger in the mixture. For the EtOH guest molecule in the mixture (Fig. 8), the interaction with C₂, C₃, N, and zinc atoms is decreased compared with pure molecules (Fig. 5). These changes in the position of the guest molecules in the mixture are probably related to the interactions between the guest molecules loaded into the ZIF-7 framework. Thus the interaction between the guest molecules was evaluated in follow.

Figure 9 shows the interactions between guest molecules in the structure. As shown in this Fig., the interaction between MeOH and EtOH with CO₂ guest molecules is stronger than other interactions, which is probably due to the interaction of the unbounded electron pair of CO₂ with the hydrogen atom of MeOH and EtOH guest molecules. The interaction of the MeOH and the H₂ guest molecules is shown at a low

distance (1.9 Å), which is higher than other guest molecules. Figure 9 shows that the interaction of EtOH with H₂ is weaker than the interaction between MeOH and H₂. These interactions between guest molecules in the mixture change the position of the molecules in the ZIF-7 framework compared with single guest molecules.

As the results for the mixture of guest molecules in the ZIF-7 framework shown, there is the most interaction between the molecules of CO₂, CO, and H₂ with EtOH and MeOH. Therefore, the effect of the interaction between CO₂, CO, and H₂ molecules with EtOH and MeOH on their position in the structure was investigated in a binary mixture. Figure 10 displays the RDF results for CO₂, CO, H₂, EtOH, and MeOH guest molecules in the binary mixture as a function of distance (r) with the ZIF-7 framework. The RDF results for the MeOH and CO₂ mixture show the strong interaction between MeOH and CO₂ intensifies the presence of CO₂ around the C₂ atom of the ZIF-7 framework, which has a different distribution than that of CO₂ guest molecule alone (Fig. 5) or a mixture of all molecules (Fig. 8). In addition, RDF results for H₂ and MeOH guest molecules show that the distribution of H₂ molecules in the ZIF-7 framework is strongly affected by MeOH molecules. As shown in Fig. 10, the H₂ molecules are more located around C₂ and C₄ atoms in the ZIF-7 framework if the MeOH and H₂ mixture is presented in ZIF-7. However, RDF results show that the interaction of MeOH guest molecules in the ZIF-7 framework is increased by the presence of H₂ molecules, but its distribution is not affected by CO₂ guest molecules.

The RDF results of the EtOH binary mixtures with CO₂ and H₂ show that the presence of EtOH does not have much effect on the distribution of H₂ and CO₂ guest molecules in the ZIF-7 framework. But the distribution of EtOH guest molecules in the ZIF-7 framework is affected by the presence of H₂ and CO₂ guest molecules and the interaction of EtOH with linkers and Zn atoms is decreased in presence of H₂ and CO₂ guest molecules. The difference in the distribution of MeOH and EtOH guest molecules in the ZIF-7 framework and their effect on the distribution of CO₂ and H₂ molecules can be related to the higher dipole moment of MeOH, which has a stronger effect on the presence of molecules around it.

Table 2
Diffusion results of the binary mixtures, $D_S (\times 10^{-10} \text{ m}^2/\text{s})$.

Mixture	MeOH	EtOH	CO ₂	CO	H ₂
MeOH + EtOH	0.008	0.023	-	-	-
MeOH + CO ₂	0.013	-	0.010	-	-
MeOH + CO	0.020	-	-	0.023	-
MeOH + H ₂	0.020	-	-	-	0.016
EtOH + CO ₂	-	0.010	0.008	-	-
EtOH + CO	-	0.012	-	0.006	-
EtOH + H ₂	-	0.048	-	-	2.170
CO ₂ + CO	-	-	0.038	0.025	-
CO ₂ + H ₂	-	-	0.012	-	0.023
CO + H ₂	-	-	-	0.013	0.027

The self-diffusion coefficient at equilibrium conditions (D_S) for mixed guest molecules is calculated from MSD results and is listed in Table 2. By comparing the calculated coefficients for the binary mixture (Table 2) and the pure molecules (Table 1), it is shown that the presence of molecules in the mixture affects their diffusion coefficient. The result shows that the MeOH diffusion decreased in the presence of EtOH and increased in presence of H₂ and CO. The attraction between MeOH and EtOH guest molecules in a binary mixture reduces its diffusion. Similarly, the reduction in the diffusion coefficient of other guest molecules in binary mixtures (Table 2) can be attributed to the attraction or repulsion between the guest molecules.

Conclusion

In this work, the results of adsorption and diffusion synthesis gas component in the ZIF-7 framework were presented. GCMC and NVT-MD methods were performed to evaluate the adsorption and diffusion coefficient, respectively. The Qst values show the strength of interaction energy between ZIF and guest molecules and are slightly sensitive to pressure. The results of diffusion show that the values of the self-diffusion coefficients at the initial point of the process follow this order: $D_{H_2} > D_{MeOH} > D_{CO} > D_{CO_2} > D_{EtOH}$ which depends on the kinetic diameter of the guest molecules and interaction between guest molecules and the gate of pore structures.; nonetheless, the diffusion coefficient at equilibrium condition probably depends on how the guest molecule interacts with ZIF-7 structure. The results of RDF for pure components indicate that Zn atoms are favorable adsorption sites for CO, CO₂, and H₂ gases. Also, the organic linker in ZIF-7 is the most favorable adsorption site for MeOH and EtOH guest molecules rather

than the metal cluster. The diffusion coefficient at equilibrium conditions for mixed guest molecules is affected by the presence of molecules in the mixture. Consequently, the reduction in the diffusion coefficient of other guest molecules in binary mixtures can be attributed to the attraction or repulsion between the guest molecules. The results of RDF calculated for mixture show that interactions between guest molecules in the structure change the position of the molecules in the structure.

Declarations

Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Declaration of interest statement

The authors declare that they have no conflict of interest.

References

1. S. Ghosh, V. Uday, A. Giri, S. Srinivas, Biogas to methanol: A comparison of conversion processes involving direct carbon dioxide hydrogenation and via reverse water gas shift reaction. *J. Clean. Prod.* **217**, 615–626 (2019)
2. Y.-R. Lee, M.-S. Jang, H.-Y. Cho, H.-J. Kwon, S. Kim, W.-S. Ahn, ZIF-8: A comparison of synthesis methods. *Chem. Eng. J.* **271**, 276–280 (2015)
3. F. Jensen, J. Wiley, C. Sons, *Introduction to Computational (Chemistry)*, 2007)
4. M.P. Allen, Introduction to molecular dynamics simulation. *Computational soft matter: from synthetic polymers to proteins* **23**, 1–28 (2004)
5. L. Sandström, J. Lindmark, J. Hedlund, Separation of methanol and ethanol from synthesis gas using MFI membranes. *J. Membr. Sci.* **360**, 265–275 (2010)
6. K. Zhang, L. Zhang, J. Jiang, Adsorption of C1–C4 alcohols in zeolitic imidazolate framework-8: Effects of force fields, atomic charges, and framework flexibility. *J. Phys. Chem. C* **117**, 25628–25635 (2013)
7. S. De, S. Dutta, B. Saha, Critical design of heterogeneous catalysts for biomass valorization: current thrust and emerging prospects. *Catal. Sci. Technol.* **6**, 7364–7385 (2016)
8. F. Salles, A. Ghoufi, G. Maurin, R.G. Bell, C. Mellot-Draznieks, G. Férey, Molecular Dynamics Simulations of Breathing MOFs: Structural Transformations of MIL-53 (Cr) upon Thermal Activation

- and CO₂ Adsorption. *Angew. Chem. Int. Ed.* **47**, 8487–8491 (2008)
9. F. Salles, D.I. Kolokolov, H. Jobic, G. Maurin, P.L. Llewellyn, T. Devic et al., Adsorption and diffusion of H₂ in the MOF type systems MIL-47 (V) and MIL-53 (Cr): a combination of microcalorimetry and QENS experiments with molecular simulations. *J. Phys. Chem. C* **113**, 7802–7812 (2009)
 10. A. Battisti, S. Taioli, G. Garberoglio, Zeolitic imidazolate frameworks for separation of binary mixtures of CO₂, CH₄, N₂ and H₂: A computer simulation investigation. *Microporous Mesoporous Mater.* **143**, 46–53 (2011)
 11. H. Chang, Y. Wang, L. Xiang, D. Liu, C. Wang, Y. Pan, Improved H₂/CO₂ separation performance on mixed-linker ZIF-7 polycrystalline membranes. *Chem. Eng. Sci.* **192**, 85–93 (2018)
 12. Q. Wei, D. Yang, M. Fan, H.G. Harris, Applications of nanomaterial-based membranes in pollution control. *Crit. Rev. Environ. Sci. Technol.* **43**, 2389–2438 (2013)
 13. C.-W. Tsai, E.H. Langner, R.A. Harris, Computational study of ZIF-8 analogues with electron donating and withdrawing groups for CO₂ adsorption. *Microporous Mesoporous Mater.* **288**, 109613 (2019)
 14. L.J. Murray, M. Dincă, J.R. Long, Hydrogen storage in metal–organic frameworks. *Chem. Soc. Rev.* **38**, 1294–1314 (2009)
 15. A.R. Millward, O.M. Yaghi, Metal – organic frameworks with exceptionally high capacity for storage of carbon dioxide at room temperature. *J. Am. Chem. Soc.* **127**, 17998–17999 (2005)
 16. T. Watanabe, D.S. Sholl, Accelerating applications of metal–organic frameworks for gas adsorption and separation by computational screening of materials. *Langmuir* **28**, 14114–14128 (2012)
 17. S.T. Meek, J.A. Greathouse, M.D. Allendorf, Metal-organic frameworks: A rapidly growing class of versatile nanoporous materials. *Adv. Mater.* **23**, 249–267 (2011)
 18. A.U. Czaja, N. Trukhan, U. Müller, Industrial applications of metal–organic frameworks. *Chem. Soc. Rev.* **38**, 1284–1293 (2009)
 19. G. Férey, Hybrid porous solids: past, present, future. *Chem. Soc. Rev.* **37**, 191–214 (2008)
 20. U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt, J. Pastre, Metal–organic frameworks—prospective industrial applications. *J. Mater. Chem.* **16**, 626–636 (2006)
 21. R. Babarao, Z. Hu, J. Jiang, S. Chempath, S.I. Sandler. Storage and separation of CO₂ and CH₄ in silicalite, C168 schwarzite, and IRMOF-1: a comparative study from Monte Carlo simulation. *Langmuir* 2007,**23**:659–666
 22. A.I. Skoulidas, D.S. Sholl, Self-diffusion and transport diffusion of light gases in metal-organic framework materials assessed using molecular dynamics simulations. *J. Phys. Chem. B* **109**, 15760–15768 (2005)
 23. N. Rosenbach Jr., A. Ghoufi, I. Deroche, P. Llewellyn, T. Devic, S. Bourrelly et al., Adsorption of light hydrocarbons in the flexible MIL-53 (Cr) and rigid MIL-47 (V) metal–organic frameworks: a combination of molecular simulations and microcalorimetry/gravimetry measurements. *Physical Chemistry Chemical Physics* **12**, 6428–6437 (2010)

24. J.-R. Li, R.J. Kuppler, H.-C. Zhou, Selective gas adsorption and separation in metal–organic frameworks. *Chem. Soc. Rev.* **38**, 1477–1504 (2009)
25. S. Keskin, T.M. van Heest, D.S. Sholl, Can metal–organic framework materials play a useful role in large-scale carbon dioxide separations? *ChemSusChem* 2010,3:879–891
26. J. Lee, O.K. Farha, J. Roberts, K.A. Scheidt, S.T. Nguyen, J.T. Hupp, Metal–organic framework materials as catalysts. *Chem. Soc. Rev.* **38**, 1450–1459 (2009)
27. L. Ma, C. Abney, W. Lin, Enantioselective catalysis with homochiral metal–organic frameworks. *Chem. Soc. Rev.* **38**, 1248–1256 (2009)
28. J. Seo, D. Whang, H. Lee, S. Jun, J. Oh, Y. Jeon et al. *Nature* 2000, 404, 982 – 986. [Crossref], [PubMed], [CAS], [Google Scholar] (b) Evans, OR; Ngo, HL; Lin, W. *J. Am. Chem. Soc* 2001, **123**:10395–10396
29. L.B. Vilhelmsen, K.S. Walton, D.S. Sholl, Structure and mobility of metal clusters in MOFs: Au, Pd, and AuPd clusters in MOF-74. *J. Am. Chem. Soc.* **134**, 12807–12816 (2012)
30. K. Leus, M. Vandichel, Y.-Y. Liu, I. Muylaert, J. Musschoot, S. Pyl et al., The coordinatively saturated vanadium MIL-47 as a low leaching heterogeneous catalyst in the oxidation of cyclohexene. *J. Catal.* **285**, 196–207 (2012)
31. J. Rocha, L.D. Carlos, F.A.A. Paz, D. Ananias, Luminescent multifunctional lanthanides-based metal–organic frameworks. *Chem. Soc. Rev.* **40**, 926–940 (2011)
32. S. Keskin, S. Kızılel, Biomedical applications of metal organic frameworks. *Industrial & Engineering Chemistry Research* **50**, 1799–1812 (2011)
33. L.E. Kreno, K. Leong, O.K. Farha, M. Allendorf, R.P. Van Duyne, J.T. Hupp, Metal–organic framework materials as chemical sensors. *Chemical reviews* **112**, 1105–1125 (2011)
34. K.S. Park, Z. Ni, A.P. Côté, J.Y. Choi, R. Huang, F.J. Uribe-Romo, *et al.* Exceptional chemical and thermal stability of zeolitic imidazolate frameworks. *Proceedings of the National Academy of Sciences* 2006, **103**:10186–10191
35. H. Hayashi, A.P. Cote, H. Furukawa, M. O’Keeffe, O.M. Yaghi, Zeolite A imidazolate frameworks. *Nat. Mater.* **6**, 501 (2007)
36. Y.Q. Tian, C.X. Cai, X.M. Ren, C.Y. Duan, Y. Xu, S. Gao et al., The Silica-Like Extended Polymorphism of Cobalt (II) Imidazolate Three-Dimensional Frameworks: X-ray Single-Crystal Structures and Magnetic Properties. *Chemistry–A European Journal* **9**, 5673–5685 (2003)
37. Y.Q. Tian, Y.M. Zhao, Z.X. Chen, G.N. Zhang, L.H. Weng, D.Y. Zhao, Design and generation of extended zeolitic metal–organic frameworks (ZMOFs): synthesis and crystal structures of zinc (II) imidazolate polymers with zeolitic topologies. *Chemistry–A European Journal* **13**, 4146–4154 (2007)
38. F. Wendler, L.-N. Todi, F. Meister, Thermostability of imidazolium ionic liquids as direct solvents for cellulose. *Thermochimica acta* **528**, 76–84 (2012)
39. R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O’Keeffe et al., High-throughput synthesis of zeolitic imidazolate frameworks and application to CO₂ capture. *Science* **319**, 939–943 (2008)

40. L. Hertäg, H. Bux, J. Caro, C. Chmelik, T. Remsungnen, M. Knauth et al., Diffusion of CH₄ and H₂ in ZIF-8. *J. Membr. Sci.* **377**, 36–41 (2011)
41. J. van den Bergh, C. Gücüyener, E.A. Pidko, E.J. Hensen, J. Gascon, F. Kapteijn, Understanding the anomalous alkane selectivity of ZIF-7 in the separation of light alkane/alkene mixtures. *Chemistry–A European Journal* **17**, 8832–8840 (2011)
42. C. Gücüyener, J. van den Bergh, J. Gascon, F. Kapteijn, Ethane/ethene separation turned on its head: selective ethane adsorption on the metal – organic Framework ZIF-7 through a gate-opening mechanism. *J. Am. Chem. Soc.* **132**, 17704–17706 (2010)
43. T. Xiao, D. Liu, Progress in the synthesis, properties and applications of ZIF-7 and its derivatives. *Materials Today Energy* **14**, 100357 (2019)
44. M. Zhou, Q. Wang, L. Zhang, Y.-C. Liu, Y. Kang, Adsorption sites of hydrogen in zeolitic imidazolate frameworks. *J. Phys. Chem. B* **113**, 11049–11053 (2009)
45. D. Liu, C. Zheng, Q. Yang, C. Zhong, Understanding the adsorption and diffusion of carbon dioxide in zeolitic imidazolate frameworks: a molecular simulation study. *J. Phys. Chem. C* **113**, 5004–5009 (2009)
46. R.B. Rankin, J. Liu, A.D. Kulkarni, J.K. Johnson, Adsorption and diffusion of light gases in ZIF-68 and ZIF-70: a simulation study. *J. Phys. Chem. C* **113**, 16906–16914 (2009)
47. R. Babarao, J. Jiang, Unprecedentedly high selective adsorption of gas mixtures in rho zeolite-like metal – organic framework: a molecular simulation study. *J. Am. Chem. Soc.* **131**, 11417–11425 (2009)
48. B. Liu, B. Smit, Comparative molecular simulation study of CO₂/N₂ and CH₄/N₂ separation in zeolites and metal – organic frameworks. *Langmuir* **25**, 5918–5926 (2009)
49. B. Liu, B. Smit, Molecular simulation studies of separation of CO₂/N₂, CO₂/CH₄, and CH₄/N₂ by ZIFs. *J. Phys. Chem. C* **114**, 8515–8522 (2010)
50. Z. Bao, S. Alnemrat, L. Yu, I. Vasiliev, Q. Ren, X. Lu et al., Adsorption of ethane, ethylene, propane, and propylene on a magnesium-based metal–organic framework. *Langmuir* **27**, 13554–13562 (2011)
51. M. Rahmati, H. Modarress, Selectivity of new siliceous zeolites for separation of methane and carbon dioxide by Monte Carlo simulation. *Microporous Mesoporous Mater.* **176**, 168–177 (2013)
52. T. Chokbunpiam, S. Fritzsche, C. Chmelik, J. Caro, W. Janke, S. Hannongbua, Gate opening, diffusion, and adsorption of CO₂ and N₂ mixtures in ZIF-8. *J. Phys. Chem. C* **120**, 23458–23468 (2016)
53. C. Wang, B. Li, Y. Wang, Z. Xie, Insight into the topology effect on the diffusion of ethene and propene in zeolites: A molecular dynamics simulation study. *Journal of Energy Chemistry* **22**, 914–918 (2013)
54. P. Krokidas, S. Moncho, E.N. Brothers, I.G. Economou, Defining new limits in gas separations using modified ZIF systems. *ACS Appl. Mater. Interfaces.* **12**, 20536–20547 (2020)
55. B. Bayati, A. Ghorbani, K. Ghasemzadeh, A. Iulianelli, A. Basile, Study on the Separation of H₂ from CO₂ Using a ZIF-8 Membrane by Molecular Simulation and Maxwell-Stefan Model. *Molecules* **24**, 4350 (2019)

56. X. Wu, J. Huang, W. Cai, M. Jaroniec, Force field for ZIF-8 flexible frameworks: atomistic simulation of adsorption, diffusion of pure gases as CH₄, H₂, CO₂ and N₂. *RSC Advances* **4**, 16503–16511 (2014)
57. B. Liu, Q. Yang, C. Xue, C. Zhong, B. Smit, Molecular simulation of hydrogen diffusion in interpenetrated metal–organic frameworks. *Physical chemistry chemical physics* **10**, 3244–3249 (2008)
58. C. Lee, W. Yang, R.G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Physical review B* **37**, 785 (1988)
59. P. Zhao, G.I. Lampronti, G.O. Lloyd, M.T. Wharmby, A.K. Facq Sb, Cheetham et al., Phase transitions in zeolitic imidazolate framework 7: the importance of framework flexibility and guest-induced instability. *Chem. Mater.* **26**, 1767–1769 (2014)
60. F. Salles, H. Jobic, T. Devic, P.L. Llewellyn, C. Serre, G. Férey et al., Self and transport diffusivity of CO₂ in the metal – organic framework MIL-47 (v) explored by quasi-elastic neutron scattering experiments and molecular dynamics simulations. *ACS Nano* **4**, 143–152 (2010)
61. K. Zhang, R.P. Lively, J.D. Noel, M.E. Dose, B.A. McCool, R.R. Chance et al., Adsorption of water and ethanol in MFI-type zeolites. *Langmuir* **28**, 8664–8673 (2012)
62. K. Zhang, R.P. Lively, M.E. Dose, A.J. Brown, C. Zhang, J. Chung et al., Alcohol and water adsorption in zeolitic imidazolate frameworks. *Chem. Commun.* **49**, 3245–3247 (2013)
63. P. Zhao, H. Fang, S. Mukhopadhyay, A. Li, S. Rudić, I.J. McPherson et al., Structural dynamics of a metal–organic framework induced by CO₂ migration in its non-uniform porous structure. *Nature communications* **10**, 1–8 (2019)
64. Z. Yang, L. Liu, T. Gui, C.X. Zhou Rf, Mean Residence Time of CO₂ Molecules in Flexible ZIF-8 Cages Explored by Molecular Dynamics Simulations. *Chin. J. Chem. Phys.* **26**, 553 (2013)
65. J. Pérez-Pellitero, H. Amrouche, F.R. Siperstein, G. Pirngruber, C. Nieto-Draghi, G. Chaplais et al., Adsorption of CO₂, CH₄, and N₂ on zeolitic imidazolate frameworks: experiments and simulations. *Chemistry–A European Journal* **16**, 1560–1571 (2010)
66. A. Golchoobi, H. Pahlavanzadeh, Molecular simulation, experiments and modelling of single adsorption capacity of 4A molecular sieve for CO₂–CH₄ separation. *Sep. Sci. Technol.* **51**, 2318–2325 (2016)
67. A.M. Mosier, H.L. Larson, E.R. Webster, M. Ivos, F. Tian, L. Benz, Low-temperature adsorption and diffusion of methanol in ZIF-8 nanoparticle films. *Langmuir* **32**, 2947–2954 (2016)
68. K. Zhang, R.P. Lively, C. Zhang, W.J. Koros, R.R. Chance, Investigating the intrinsic ethanol/water separation capability of ZIF-8: an adsorption and diffusion study. *J. Phys. Chem. C* **117**, 7214–7225 (2013)
69. I. Khay, G. Chaplais, H. Nouali, C. Marichal, J. Patarin, Water intrusion–extrusion experiments in ZIF-8: impacts of the shape and particle size on the energetic performances. *RSC Advances* **5**, 31514–31518 (2015)

70. K.M. Thomas, Adsorption and desorption of hydrogen on metal–organic framework materials for storage applications: comparison with other nanoporous materials. *Dalton transactions* 2009:1487–1505
71. R. Babarao, J. Jiang, Molecular screening of metal – organic frameworks for CO₂ storage. *Langmuir* **24**, 6270–6278 (2008)
72. L. Xiang, D. Liu, H. Jin, L.-W. Xu, C. Wang, S. Xu et al., Locking of phase transition in MOF ZIF-7: improved selectivity in mixed-matrix membranes for O₂/N₂ separation. *Mater. Horiz.* **7**, 223–228 (2020)
73. Y. Du, B. Wooler, M. Nines, P. Kortunov, C.S. Paur, J. Zengel et al., New high-and low-temperature phase changes of ZIF-7: elucidation and prediction of the thermodynamics of transitions. *J. Am. Chem. Soc.* **137**, 13603–13611 (2015)
74. X. Yang, A. Arami-Niya, G. Xiao, E.F. May. Flexible Adsorbents at High Pressure: Observations and Correlation of ZIF-7 Stepped Sorption Isotherms for Nitrogen, Argon, and Other Gases. *Langmuir* 2020,**36**:14967–14977
75. S. Rahman, A. Arami-Niya, X. Yang, G. Xiao, G.K. Li, E.F. May, Temperature dependence of adsorption hysteresis in flexible metal organic frameworks. *Communications Chemistry* **3**, 1–6 (2020)

Figures

Figure 1

ZIF-7 framework with zinc atoms connected through benzimidazolate (blm) linkers in tetrahedral coordination and include two six-member-ring pores (pore A and B) and one four-member ring-type pore.

Figure 2

The EP distribution of zinc atoms connected by blm linkers. EP increases with the color order: blue-white-red

Figure 3

The density of guest molecules in the ZIF-7 framework at low pressure (left column) and high pressure (right column).

Figure 4

MSD of the single guest molecules (16 molecules per unit cell).

Figure 5

The label of the studied atoms in the ZIF-7 structure and calculated RDF ($g(r)$) results of the single guest molecules as a function of distance (r).

Figure 6

The adsorption isotherm of pure guest molecules.

Figure 7

The adsorption Qst for pure guest molecules at 300 K

Figure 8

The calculated RDF ($g(r)$) results of the mixture guest molecules (29%CO, 3%CO₂, 58%H₂, 8%MeOH, 2%EtOH) in the ZIF-7 framework as a function of distance (r).

Figure 9

The calculated RDF ($g(r)$) results between guest molecules for mixture guest molecules (29%CO, 3%CO₂, 58%H₂, 8%MeOH, 2%EtOH) in ZIF-7 framework as a function of distance (r).

Figure 10

The calculated RDF ($g(r)$) results between guest molecules for binary guest molecules in the ZIF-7 framework as a function of distance (r).